J. Chem. Eng. Data **2000,** *45,* 75−77 **75**

Effect of Cosolvent and Nonionic Surfactant on Partition Coefficient of Azadirachta Indica A. Juss. (Neem) Seed Oil in Water−Hexane at (298.15, 303.15, 308.15, and 313.15) K

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The partition coefficient of Azadirachta Indica A. Juss. (neem) seed oil (NSO) in water + hexane was calculated by measuring the amount of NSO concentration in hexane by a UV spectrophotometric method at (298.15, 303.15, 308.15, and 313.15) K. The partition coefficients of NSO increased with an increasing amount of NSO, which indicates a hydrophobic interaction of NSO in the organic phase. Addition of cosolvent (methanol) or nonionic surfactant (polysorbate-80) to the water + hexane mixture decreased the partition coefficient of NSO in the temperature interval studied.

Introduction

Azadirachta Indica A. Juss., commonly known as the “neem” tree, produces seeds which can be extracted to get neem seed oil (NSO), which has proven its advantages over many synthetic pesticides (Aminabhavi et al., 1998 and 1999; Dave et al., 1999). The chemical structure of Azadirachtin is given in our earlier paper (Kulkarni et al., 1999). NSO is hydrophobic in nature, and hence its solubility and partition coefficient data are important in both its formulation studies and the method of application. The solubility of NSO in hexane is much higher than that in water (Kulkarni et al., 1999); thus, no NSO is found in water without adding any cosolvent or surfactant in a water + hexane system. In our previous study (Kulkarni et al., 1999), a less water soluble NSO was made soluble by adding a cosolvent or a surfactant for easier formulation. Commercially, NSO-containing formulations are available as a liquid spray to control pests such as aphids, jassids, thrips, mites, helopelties, and so forth. However, recently Kausalya et al. (1997) have reported that a NSO formulation containing a surfactant is less efficient than pure NSO. This indicates that the hydrophobicity of NSO is important for its improved action because its penetration into the pest increases with an increasing hydrophobicity. To investigate this effect further, we have chosen to study the partition coefficient of NSO in a water + hexane mixture in the presence of a cosolvent (methanol) and a nonionic surfactant (polysorbate-80). These data are presented at 298.15, 303.15, 308.15, and 313.15 K.

Experimental Section

An 80 mass % pure technical grade NSO (calculated by considering the azadirachtin concentration in NSO) was procured from Mangalwadkar Industries, Bijapur, India (courtesy of Prof. B. S. Patil). Methanol (HPLC grade), hexane (AR grade), and polysorbate-80 (Tween-80) were purchased from s.d. Fine Chemicals, Mumbai, India. Doubly distilled water was used, and its purity was checked by comparing its density and conductivity at 25 °C with the literature values, which closely agreed.

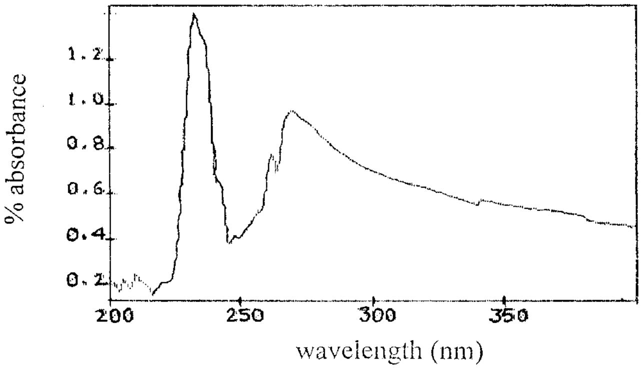

Figure 1. UV absorption spectrum of NSO in hexane.

Water + hexane mixtures were prepared by mixing exactly measured amounts (i.e., 50 mL of both the solvents) in a 100 mL volumetric flask. In the case of (methanol + water) in hexane and (polysorbate-80 + water) in hexane, the previously prepared methanol + water or polysorbate-80 + water mixtures were taken in the same quantity instead of pure water. Methanol + water mixtures were prepared by mixing the known volumes of methanol and water in a 100 mL volumetric flask. The amount of methanol transferred was calculated by subtracting the empty mass of the flask from the total mass of the volumetric flask + methanol. The polysorbate-80 + water mixtures were prepared by mass, that is, by adding the calculated mass of polysorbate-80 in 100 mL of water. The mass measurements were done on a single pan Mettler microbalance (Model AE 240, Switzerland) within an accuracy ±0.01 mg.

In each of these flasks, 1 mg of NSO was added, and the mixtures were shaken thoroughly for 5 min at each temperature and then allowed to stand for 30 min to attain equilibrium. The two phases were separated completely. The flasks were immersed in a stirred circulation, constant-temperature water bath (Grants, Model Y14, U.K.) whose temperature was maintained at (298.15, 303.15, 308.15, and 313.15) K within an accuracy ±0.1 °C at the desired temperature on a digital display.

A 10 mL aliquot of hexane was taken out from the organic layer and diluted with the same system, and the

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10.1021/je990121i CCC: $19.00

Table 1. Effect of NSO Concentration on Its Partition Coefficient at 298.15 K

NSO added/mg	amount of NSO in organic phase/(μg/mL)	amount of NSO in aqueous phase/(μg/mL)	partition coefficient
	50 mass % methanol in water + hexane		
0.571	290	281	1.032
1.014	716	298	2.403
1.520	1205	315	3.825
2.047	1700	347	4.899
	0.1 mass % polysorbate-80 in water + hexane		
0.493	400	93	4.301
1.031	1207	114	10.587
1.491	1380	111	12.432
2.003	1885	118	15.974

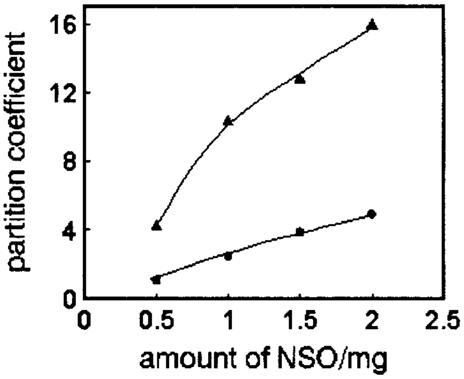

Figure 2. Effect of NSO concentration on the partition coefficient of NSO at 298.15 K in 50% methanol in water + hexane (●) and 0.1% polysorbate-80 in water + hexane (▲) systems.

Table 2. Effect of Methanol Concentration in Water on the Partition Coefficient of 1 mg of NSO at Different Temperatures

mass %	amount of NSO in organic phase/(μg/mL) at *T*/K				partition coefficient at *T*/K			
methanol	298.15	303.15	308.15	313.15	298.15	303.15	308.15	313.15
20.12	819	789	781	777	4.524	3.739	3.566	3.484
40.20	739	712	689	687	2.831	2.472	2.215	2.194
60.36	685	682	675	669	2.177	2.160	2.076	2.021
80.12	619	488	479	471	1.626	0.953	0.919	0.890

Table 3. Effect of Polysorbate-80 Concentration in Water on the Partition Coefficient of 1 mg of NSO at Different Temperatures

mass % poly-	amount of NSO in organic phase/(μg/mL) at *T*/K				partition coefficient at *T*/K			
sorbate-80	298.15	303.15	308.15	313.15	298.15	303.15	308.15	313.15
0.049	937	933	932	932	14.87	13.92	13.70	13.70
0.112	887	879	877	872	7.849	7.264	7.130	6.812
0.148	877	868	863	861	7.130	6.575	6.299	6.194
0.203	870	855	851	847	6.692	5.711	5.711	5.535

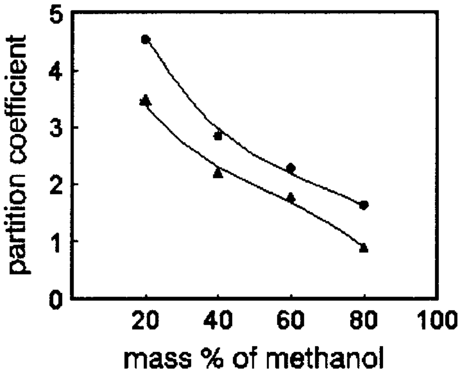

Figure 3. Effect of the methanol content in water on the partition coefficient of NSO at 298.15 K (●) and at 313.15 K (▲).

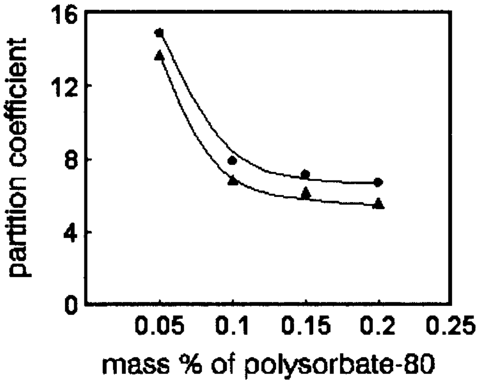

Figure 4. Effect of the polysorbate-80 content in water on the partition coefficient of NSO at 298.15 K (●) and at 313.15 K (▲).

absorbance was measured at 232 nm using a UV spectrophotometer (Anthelie, Secomam, France). See Figure 1. The peak observed at 232 nm was used for the assay studies. The standard curve for NSO was established using hexane at 232 nm. The absorbance values taken at 232 nm of NSO with respect to its concentration were plotted to obtain a straight line with a correlation coefficient of 0.998. The slope of the line was calculated by the least-squares procedure, and these values were used for further calculations.

Results and Discussion

The partition coefficient values of NSO were calculated by taking the ratio of the NSO content in the organic phase to that in the aqueous phase. The results of partition coefficients calculated for the addition of different amounts of NSO to 50% methanol water + hexane and to (0.1% polysorbate water) + hexane at 298.15 K are presented in Table 1 and displayed in Figure 2. It is observed that, with an increasing concentration of NSO in the mixture, the partition coefficient also increases. This is attributed to the limited solubility of NSO in the aqueous phase as well as the hydrophobic interaction of NSO in the organic phase.

The results of NSO partition coefficients after the addition of methanol and polysorbate-80 to the aqueous phase at four temperatures are presented in Tables 2 and 3, respectively. These data are also displayed in Figures 3 and 4. When 20−80 mass % methanol in water and 0.05−0.20 mass % polysorbate-80 in water were added, a decrease in the NSO partition coefficient was observed with an increasing concentration of both methanol and polysorbate-80 in the water phase at all the temperatures. This may be due to an increased solubility of NSO in the aqueous phase after the addition of methanol or polysorbate-80 (Kulkarni et al., 1999). However, the increased solubility of NSO in the aqueous phase after the addition of methanol is probably due to the increased organic nature of the aqueous phase, whereas polysorbate-80 might reduce the surface tension of NSO. In all the cases, the partition coefficient data of NSO show a decrease with an increasing temperature.

In conclusion, the present results show that 20 mass % methanol in water yields a lower partition coefficient than 0.2 mass % polysorbate-80; that is, 20 mass % methanol has a stronger effect than 0.2 mass % polysorbate-80. It appears that we require much less polysorbate-80 than methanol to obtain a dramatic reduction in the partition coefficient. Also, the partition coefficient reaches a nearly constant value around 6 at a polysorbate-80 concentration above 0.2 mass %. With methanol, the partition coefficient values continue to decrease to values below 1 as the methanol content increases. Clearly, the effect depends on the amount of cosolvent or surfactant added in the actual formulations. Further experiments on NSO formulations are being presently carried out in our laboratory.

Literature Cited

Aminabhavi, T. M.; Kulkarni, A. R.; Soppimath, K. S.; Balundgi, R. H.; Mehta, M. H.; Dave, A. M. Polymeric Controlled Release Devices in Agriculture. *Polym. News* **1998**, *23*, 246−247.

Dave, A. M.; Mehta, M. H.; Aminabhavi, T. M.; Kulkarni, A. R.; Soppimath, K. S. A Review on Controlled Release of Nitrogen Fertilizers Through Polymeric Membrane Devices. *Polym.-Plast. Technol. Eng.* **1999**, *38*, 673−709.

Kulkarni, A. R.; Soppimath, K. S.; Aminabhavi, T. M.; Dave, A. M.; Mehta, M. H. Urea-Formaldehyde Cross-linked Starch and Guar [Azadirachta Indica A. Juss. (Neem) Seed Oil]: Swelling and Release Kinetics. *J. Appl. Polym. Sci.* **1999a**, *73*, 2437−2446.

Kulkarni, A. R.; Soppimath, K. S.; Aminabhavi, T. M. Solubility Study of Azadirachta Indica A. Juss. (Neem) Seed Oil in the Presence of Cosolvent/Nonionic Surfactant at (298.15, 303.15, 308.15, and 313.15) K. *J. Chem. Eng. Data* **1999b**, *44*, 836−838.

Kausalya, K. G.; Srinivasan, K.; Chelliah, S. Evaluation of Few Neem Formulations Against American Bollworm (H. Armigera Hub.) in Cotton. *Pestology* **1997**, *21*, 5−8.

Received for review May 1, 1999. Accepted October 7, 1999. The authors are thankful to the Council of Scientific and Industrial Research (Grant No. 80(0025)/97/EMR-II), New Delhi, for financial support. K.S.S. was supported as a senior CSIR research fellow, and A.R.K. was supported by the GSFC Science Foundation, Vadodara, under the University-Industry Interactive Program of Research.

JE990121I