Solubility of Various Hydrocarbons in Aqueous Solutions of Sodium *p*-Cymenesulfonate and 1-Butanol[†]

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Miscibilities of various hydrocarbons in systems containing 1-butanol and aqueous solutions of sodium *p*-cymenesulfonate (sodium 2-methyl-5-(1-methylethyl)benzenesulfonate) (2.5 mol/kg H_2O) have been determined at 25 °C. The hydrocarbons included aliphatic hydrocarbons C_nH_{2n+2} (n = 6–11, 15), cyclohexane, aromatic hydrocarbons $C_6H_5C_nH_{2n+1}$ (n = 0–2, 4, 6–10), and various hydrocarbon mixtures. The amount of 1-butanol required to achieve miscibility increases with increasing chain length of the aliphatic hydrocarbons and with increasing number of alkyl carbons on the benzene ring of the aromatic hydrocarbons. The two-phase region with cyclohexane is smaller than with hexane and similar to that with butylbenzene. For mixtures of two hydrocarbons the amount of 1-butanol required (at a hydrocarbon–aqueous solution ratio of 1:1) seems to vary linearly with weight fraction of the hydrocarbon components.

In a study of miscibilities of aqueous–hydrocarbon systems in the presence of cosolvents, we have recently completed a report on compositions at boundaries between one and two liquid phases for toluene and aqueous solutions of nine alkyl-substituted benzenesulfonates, in the presence of 1-butanol (*1*). The alkyl groups on the sulfonates were smaller than those of the size usually thought to cause micellization in aqueous solutions. Here we report phase boundary curves for systems containing 1-butanol, aqueous solutions of one of these sulfonates, sodium *p*-cymenesulfonate (sodium 2-methyl-5-(1-methylethyl)-benzenesulfonate), and a number of alkanes, alkyl-substituted benzenes, and hydrocarbon mixtures. As before, the four(or five)-component systems will be treated as three-component systems by fixing the ratio of aromatic sulfonate to water (or in addition the ratio of the hydrocarbons in mixtures). The molality, m, of the aqueous component was throughout 2.5 mol of sulfonate/kg of water. Our motivation continues to be accumulation of information which may help elucidate the chemistry underlying the systems containing long-chain alkyl benzenesulfonate surfactants used in the micellar-flood approach to enhanced oil recovery.

Experimental Section

Benzene, toluene, and 1-butanol were certified ACS grade from Fisher Scientific Co. *p*-Xylene and *p*-cymene were from Matheson Coleman and Bell. Cyclohexane was the best grade from Eastman Co. The hexane was analytical reagent from Mallinckrodt. The hydrocarbons heptane, octane, nonane, decane, undecane, pentadecane, 1-phenylhexane, 1-phenylheptane, 1-phenyloctane, 1-phenylnonane, and 1-phenyldecane were the best grades obtainable from Aldrich Chemical Co., Inc. All these chemicals were used without further purification. Sodium *p*-cymenesulfonate was synthesized as described before (*2*).

The phase boundary curves were determined by a weight titration procedure (*1*). The titrations were carried out at 25 ± 0.1 °C. The titrant (1-butanol) was added from a syringe to 8-mL test tubes with screw-on, Teflon-lined caps, containing 0.5–1.0 mL of mixtures of the hydrocarbons and aqueous solution. The end point was indicated by the disappearance of the second liquid phase. The pseudoternary diagrams are plotted as weight percent on triangular graphs with the aqueous component taken to be 2.5 m sodium *p*-cymenesulfonate.

Results and Discussion

Compositions of the boundaries between one and two liquid phases for four-component systems containing one of the 17 hydrocarbons, 1-butanol, and 2.5 m solutions of sodium *p*-cymenesulfonate are summarized in Table I. They are presented graphically in Figure 1 for alkanes and in Figure 2 for alkyl-substituted benzenes. The one-phase region is at the top of the graphs, adjacent to the 1-butanol apex. The figures also include, for comparison, the phase boundary curve for the water–toluene–1-butanol system (*3*). It should be typical of the other hydrocarbon–water–1-butanol systems since the point on the 1-butanol–water edge of the diagram is, of course, independent of the hydrocarbon and since the curves will also have to go essentially to the hydrocarbon corner.

With alkanes from hexane to pentadecane, the amount of 1-butanol required to produce miscibility increases as the chain length increases. With aromatic hydrocarbons the amount of 1-butanol required to produce miscibility increases with increasing number of alkyl carbons, N_{AC}, on the benzene ring.

These trends are perhaps clearer in Figure 3, in which the amount of 1-butanol required to achieve miscibility for 1:1 weight ratio of hydrocarbon to aqueous 2.5 m sodium *p*-cymenesulfonate is plotted against the number of alkyl carbons either of 1-alkanes or on substituents on benzene. For alkylbenzenes, values fall close (within 3% 1-butanol) to a smooth curve of gradually increasing slope. For these alkylbenzenes with relatively low values of N_{AC}, it seems unimportant if the alkyl carbons are all in a chain substituted at a single position (open triangles) or are distributed in more than one group (xylene and cymene, circles with bar). For alkanes, the value for hexane is close to that of the aromatic compound with the same N_{AC}, hexylbenzene, but there is little change between hexane and octane. For higher hydrocarbons, the increase in percent 1-butanol required for miscibility parallels the increase for alkylbenzenes. The point for cyclohexane falls significantly below these curves.

Increasing the number of alkyl carbons on benzenesulfonates was shown (*1*) to decrease the amount of 1-butanol required for miscibility for a given hydrocarbon (toluene), whereas the results here indicate that increasing the number of alkyl carbons in the hydrocarbons increases the amount of alcohol required for miscibility. This asymmetry is demonstrated in Figure 4, in which a comparison is made between systems containing toluenesulfonate (N_{AC} = 1) (from ref 1) and cymene (N_{AC} = 4) on the one hand and cymenesulfonate and toluene on the other.

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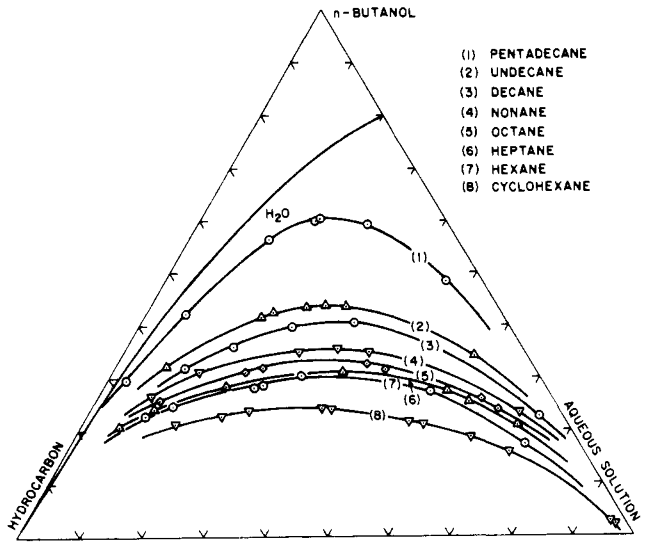

Figure 1. Phase relationships of several hydrocarbon–1-butanol–2.5 *m* aqueous sodium *p*-cymenesulfonate systems (25 °C).

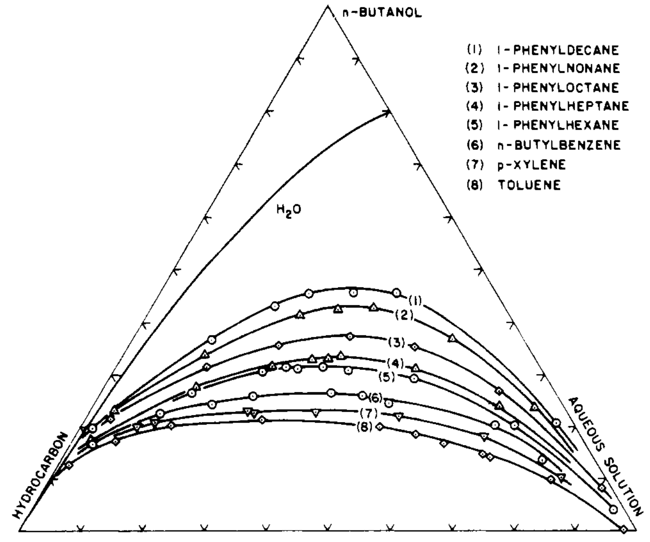

Figure 2. Phase relationships of several alkylbenzene–1-butanol–2.5 *m* aqueous sodium *p*-cymenesulfonate systems (25 °C).

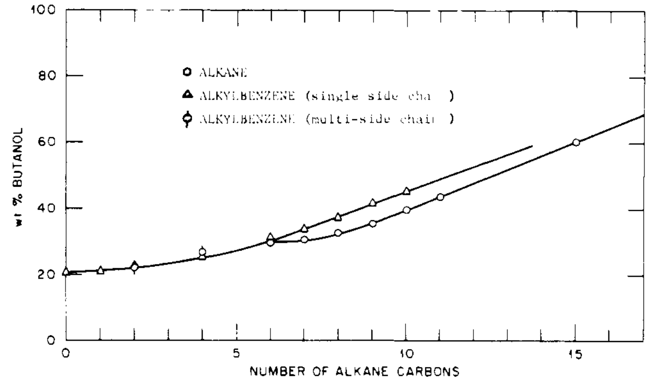

Figure 3. Minimum amount of 1-butanol required to produce miscibility at 1:1 wt % alkane (alkylbenzene) 2.5 *m* aqueous sodium *p*-cymenesulfonate.

Much less 1-butanol is required for miscibility in the second case.

Although the analogy is not perfect, the parallel of trends reported here with observations (*4*) at the University of Texas is close enough to be worth mentioning. Specifically, they have observed sharp minima of interfacial tensions between hydrocarbons and aqueous solutions of petroleum sulfonate surfactants (as well as with pure long-chain alkyl benzenesulfonates (*5*)) as a function of the size of the hydrocarbons. These minima, which can be orders of magnitude lower than for hydrocarbons of one or two carbons more or less, appear to depend primarily

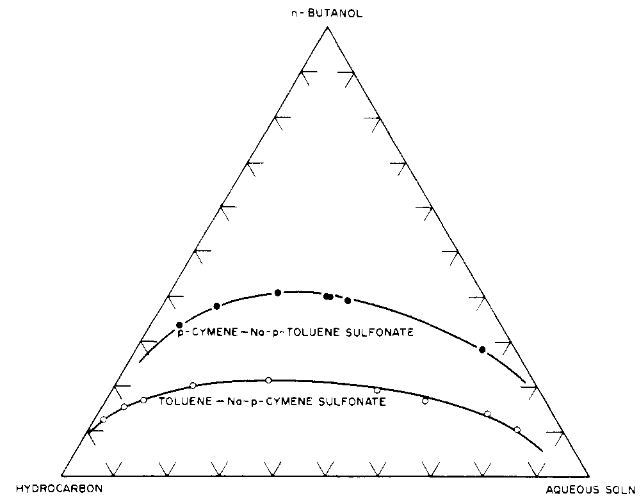

Figure 4. Comparison of 1-butanol systems containing (*p*-cymene–2.5 *m* sodium *p*-toluenesulfonate) and (toluene–2.5 *m* sodium *p*-cymenesulfonate).

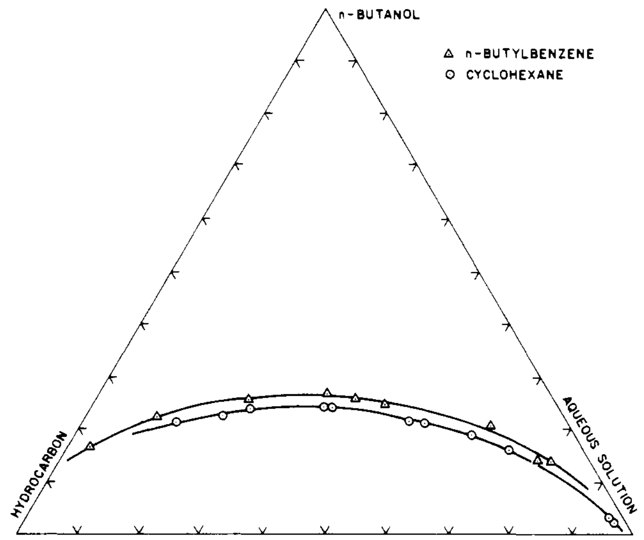

Figure 5. Aqueous sodium *p*-cymenesulfonate solution–1-butanol–1-butylbenzene and -cyclohexane systems (25 °C).

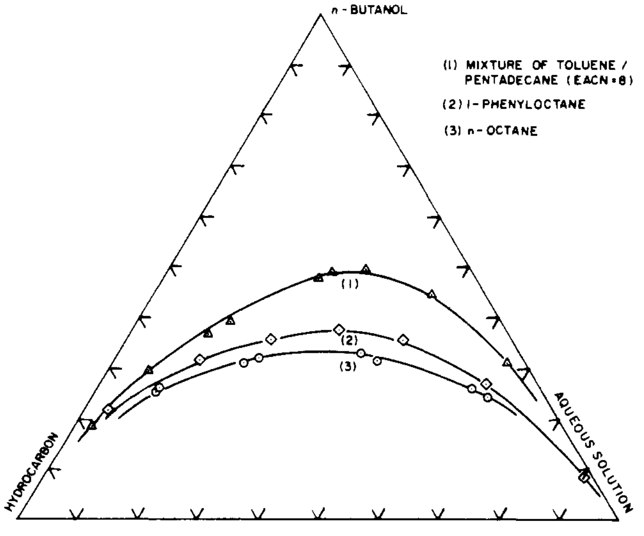

Figure 6. Phase relationships of several hydrocarbon–1-butanol–2.5 *m* aqueous sodium *p*-cymenesulfonate systems (25 °C).

Table I. Compositions of 1-Butanol-2.5 *m* Aqueous Sodium *p*-Cymenesulfonate-Hydrocarbon Systems at Boundaries between One and Two Liquid Phases (25 °C)

	wt %				wt %				wt %		
hydrocarbon	hydrocarbon	1-butanol	solution	hydrocarbon	hydrocarbon	1-butanol	solution	hydrocarbon	hydrocarbon	1-butanol	solution
hexane	9.0	17.3	73.7	decane	3.8	22.7	73.5	benzene	17.1	15.1	67.8
	19.1	27.6	53.3		24.6	40.0	33.4		32.0	19.9	48.1
	38.5	30.7	30.8		24.8	40.7	34.5		49.0	20.3	30.7
	45.5	28.7	25.8		35.3	39.4	25.3		63.9	19.7	16.4
	47.3	28.2	24.5		46.8	35.7	17.5		67.8	19.9	12.3
	62.3	24.7	13.0		56.7	31.8	11.5		77.2	17.1	5.7
	67.3	23.4	9.3		85.4	11.8	2.8	toluene[a]	2.0	0	98.0
heptane	8.6	21.2	70.2	undecane	8.5	34.1	57.4		8.5	10.1	81.4
	13.7	25.6	60.7		24.5	43.6	31.9		12.2	14.1	73.7
	16.3	27.2	56.5		28.1	43.4	28.5		16.9	14.1	69.0
	29.1	30.9	40.0		39.0	43.4	75.7		17.8	14.4	67.8
	31.5	31.2	37.3		37.1	42.4	20.5		23.0	16.6	60.4
	51.8	28.5	19.7		39.5	41.1	19.4		26.3	18.5	55.2
	65.4	24.4	10.2		59.3	32.3	8.4		30.6	19.2	50.2
	72.9	21.8	5.3	pentadecane	6.2	48.4	45.4		50.1	21.1	28.8
octane	10.0	24.3	65.7		13.3	59.2	27.5		65.2	20.2	14.6
	11.6	26.0	62.4		20.3	60.2	19.5		76.1	16.8	7.1
	24.7	31.8	43.5		21.3	59.7	19.0		80.5	15.5	4.0
	26.8	32.6	40.6		30.5	56.4	13.1		85.5	12.9	1.6
	44.2	31.7	24.1		51.0	42.2	6.8	*p*-xylene	7.9	9.5	82.6
	47.2	31.3	21.5		67.1	29.5	3.4		16.0	17.6	66.4
	63.5	26.1	10.4	cyclohexane	1.9	2.3	95.8		27.9	21.4	50.7
	64.2	25.4	10.4		2.1	3.0	94.9		41.1	22.0	36.9
nonane	6.9	23.4	69.7		11.9	16.3	71.8		51.3	21.9	26.8
	25.5	35.1	39.4		16.8	19.0	64.2		51.8	22.4	25.8
	30.1	35.2	34.7		23.2	21.5	55.3		68.2	20.3	11.5
	36.7	34.6	28.7		25.5	21.7	52.8		71.5	19.5	9.0
	54.8	31.2	14.0		36.8	24.0	39.2	ethylbenzene	11.5	14.3	74.2
	64.8	26.4	8.8		38.0	24.3	37.8		24.4	19.7	55.9
	75.7	20.7	3.6		50.2	23.8	26.0		41.5	23.4	35.2
p-cymene	5.4	12.6	82.0		55.3	22.6	22.1		63.4	20.2	16.4
	9.2	13.8	77.0		63.3	21.3	15.4		73.4	18.5	8.1
	26.9	24.3	48.8		76.9	17.7	5.4	mixture[b]	3.3	31.0	65.7
	29.5	23.5	47.0	1-phenylheptane	2.0	6.2	91.8		8.9	44.6	46.5
	36.1	24.8	39.1		7.2	20.9	71.9		17.7	49.8	32.5
	45.8	24.1	30.1		10.1	23.7	66.2		23.4	48.8	27.8
	52.5	23.8	23.7		33.3	32.8	33.9		26.2	47.8	26.0
	53.1	24.6	22.3		36.1	32.9	31.0		45.0	39.3	15.7
	59.5	24.1	16.4		43.6	30.9	25.5		50.3	36.6	13.1
	71.1	21.0	7.9		58.0	27.1	14.9		63.8	29.3	6.9
	76.4	18.8	4.8		71.7	21.8	6.5		78.5	18.8	2.7
	6.7	13.3	80.0		79.9	17.3	2.8				
1-butylbenzene	8.5	14.0	77.5	1-phenyloctane	1.8	8.3	89.9				
	12.4	21.0	66.6		9.3	26.8	63.9				
	28.1	24.7	47.2		18.6	35.1	46.3				
	31.8	25.7	42.5		28.1	37.4	34.5				
	33.0	26.9	40.1		40.6	35.4	24.0				
	33.4	25.6	41.0		54.4	31.8	13.8				
	36.4	27.1	36.5		74.8	21.9	3.3				
	49.5	25.8	24.7	1-phenylnonane	4.9	23.6	71.5				
	57.1	24.3	18.6		11.6	36.6	51.8				
	66.0	22.7	11.3		21.4	42.6	36.1				
	79.8	16.8	3.4		27.5	42.2	30.3				
	1.7	4.2	94.1		33.9	41.1	25.0				
	9.8	20.2	70.0		53.3	33.5	13.2				
	21.3	29.4	49.3		73.2	22.8	4.0				
1-phenylhexane	31.4	30.6	38.0	1-phenyldecane	2.9	20.3	76.8				
	35.1	31.4	33.5		16.4	45.4	38.3				
	39.5	31.1	29.4		23.1	45.3	31.6				
	41.1	31.4	27.5		30.5	45.2	24.3				
	45.1	30.8	24.1		37.3	42.8	19.9				
	58.9	26.4	14.7		50.7	36.3	13.0				
					78.4	19.1	2.5				

[a] From ref 1. [b] Toluene/pentadecane (EACN = 8).

on the number of alkyl carbons on the hydrocarbon. Benzene rings contribute little to what they term the effective alkyl carbon number (EACN) dependence of interfacial tension, e.g., a system with a minimum for octane will also have a minimum for phenyloctane. As pointed out in Figure 3, the miscibility relationships also are very similar for alkanes and alkylbenzenes with the same N_{AC}; for $N_{AC} = 6$ they are practically indistinguishable. They find that cyclohexane has an EACN of 4; i.e., a system with a surface tension minimum with cyclohexane would also exhibit a minimum with phenylbutane. We find it an interesting coincidence that in the present phase studies cyclohexane and 1-butylbenzene are also very similar (Figure 5).

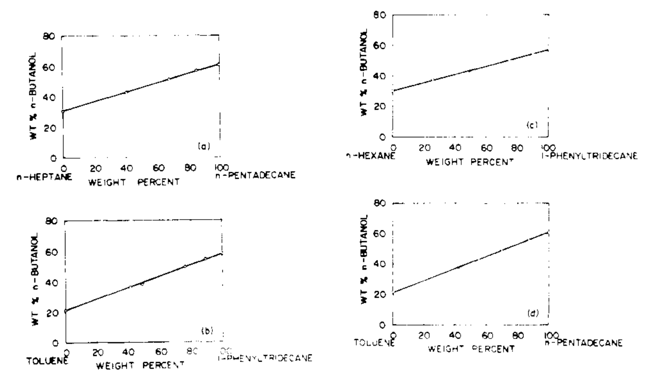

Figure 7. Miscibility relationships for hydrocarbon mixtures (wt % 1-butanol required for miscibility at 1:1 wt ratio of hydrocarbon to 2.5 *m* aqueous sodium *p*-cymenesulfonate solution; 25 °C).

The relatively simple dependence on EACN, whose applicability the Texas group demonstrated for hydrocarbon mixtures in their interfacial tension measurements, does not seem to apply to the miscibility relationships. Figure 6 compares 1-butanol–2.5 *m* cymenesulfonate systems containing octane, phenyloctane, and a 1:1 mixture of toluene and pentadecane. All three systems have, for the hydrocarbon, EACN = 8. The toluene–pentadecane system requires much more butanol for miscibility than the other two.

We were interested in establishing the basic mixing rules for the miscibility relationship. The studies were limited to the central portion of the phase diagrams where the weight ratio of hydrocarbon to aqueous cymenesulfonate solutions was one. The amount of butanol required for miscibility was established for the following four systems: hexane–pentadecane; hexane–1-phenyltridecane; toluene–pentadecane; toluene–1-phenyltridecane. The results are summarized in Figure 7. It may be noted that the amount of butanol required in all four systems varies approximately linearly with the weight fraction of one hydrocarbon in the hydrocarbon mixtures. Since some of the phase boundary diagrams are not completely symmetrical, one does not expect the linearity rule to hold generally at other hydrocarbon–aqueous ratios. However there is little doubt that the phase boundaries for the various hydrocarbon mixtures lie between those of the "pure" hydrocarbon systems.

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Excess Thermodynamic Properties of Binary Liquid Mixtures of 1,2-Dichloroethane with Normal Alkanes

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Excess volumes and isentropic compressibilities for binary liquid mixtures of 1,2-dichloroethane with hexane, heptane, octane, and nonane were determined at 303.15 K. Isothermal compressibilities were computed from isentropic compressibilities, heat capacities at constant pressure, and thermal coefficients of expansion. Excess isothermal compressibility was then calculated and the κ_T^E data were analyzed in light of both the original and modified versions of the Flory theory. The original theory fails to predict even the sign of κ_T^E while the modified theory correctly predicts the sign of κ_T^E in two systems.

A survey of the literature has shown that a number of attempts (*1*–*3*) have been made to predict excess volumes of binary liquid mixtures by using the values of the Flory interaction parameter derived from experimental excess enthalpy. Several attempts have also been made to predict excess enthalpy by employing the values of the Flory interaction parameter derived from experimental excess volume. However, very few attempts have been made to predict excess isothermal compressibility by employing the values of the interaction parameter from either experimental excess volume or excess enthalpy. These thermodynamic data have an important place in industrial and academic work. Hence an effort has been made to predict excess isothermal compressibility by using the values of the interaction parameter computed from the original Flory theory and that derived from experimental excess volumes. The mixtures studied include 1,2-dichloroethane + hexane, 1,2-dichloroethane + heptane, 1,2-dichloroethane + octane, and 1,2-dichloroethane + nonane. These mixtures have been chosen because they come under the category of *n*-alkane mixtures for which the Flory theory has been designed. The new experimental data reported here are excess volumes and isentropic compressibilities determined at 303.15 K.

Table I. Densities of the Pure Components

		ρ/g cm^{-3}	
component	temp, K	present work	lit.[5]
1,2-dichloroethane	303.15	1.238 30	1.238 31
hexane	303.15	0.650 64	0.650 70
heptane	303.15	0.675 30	0.675 38
octane	303.15	0.694 59	0.694 50
nonane	303.15	0.709 98	0.709 99

Experimental Section

Materials. 1,2-Dichloroethane, hexane, and heptane, supplied by B.D.H. Chemicals, England, and octane and nonane supplied by Veb Chemicals, West Germany, were purified by the methods