are indicative that interactions between like and unlike molecules are competitive in strength. Then sulfolane, at low concentrations, limits its role to a disturbing effect on self-association of the component (1) (positive H^E values); but with increasing sulfolane content, strond dipolar interactions between the two substances result in negative H^E values. Interactions should be more intensive in the case of benzonitrile than nitrobenzene according to a more favorable geometry of the molecule.

Registry No. Sulfolane, 126-33-0; dimethyl sulfoxide, 67-68-5; nitrobenzene, 98-95-3; bezonitrile, 100-47-0; carbon tetrachloride, 56-23-5; dioxane, 123-91-1; benzene, 71-43-2.

Literature Cited

(1) Sacco, A.; Jannelli, L. *J. Chem. Thermodyn.* **1972**, *4*, 191.
(2) Jannelli, L.; Sacco, A. *J. Chem. Thermodyn.* **1972**, *4*, 715.
(3) Sacco, A.; Inglese, A.; Ciani, P.; Dell'Atti, A.; Rakshit, A. K. *Thermochim. Acta* **1976**, *15*, 71.
(4) Jannelli, L.; Inglese, A.; Sacco, A.; Ciani, P. *Z. Naturforsch. A* **1975**, *30A*, 87.
(5) Jannelli, L.; Pansini, M. *J. Chem. Eng. Data* **1965**, *30*, 428.
(6) Jannelli, L.; Azzi, A.; Lopez, A.; Saiello, S. *J. Chem. Eng. Data* **1960**, *25*, 77.
(7) Jannelli, L.; Lopez, A.; Jalenti, R.; Silvestri, L. *J. Chem. Eng. Data* **1982**, *27*, 28.
(8) Jannelli, L.; Lopez, A.; Saiello, S. *J. Chem. Eng. Data* **1980**, *25*, 259.
(9) Riddick, A. J.; Bunger, W. B. "Techniques of Chemistry", 3rd ed.; Weissenberg, A., Ed.; Wiley Interscience: New York, 1970; Vol. II.
(10) Covington, A. K.; Dickinson, T. "Physical Chemistry of Organic Solvent Systems"; Plenum Press: London, 1973; p 244.
(11) Martinmaa, J. J. *Suom. Kemistil. B* **1969**, *42*, 33.
(12) Kiyohara, O.; Benson, G. C.; Grolier, J. P. E. *J. Chem. Thermodyn.* **1977**, *9*, 315.
(13) Karvo, M. *J. Chem. Thermodyn.* **1980**, *12*, 635.
(14) Rowlinson, J. S. "Liquids and Liquid Mixtures"; Butterworth: London, 1959; p 158.
(15) Karvo, M. *J. Chem. Thermodyn.* **1983**, *15*, 821.

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Infinite-Dilution Partition Coefficients for Haloalkane Solutes in Squalane–Dinonyl Phthalate Solvent Mixtures at 30.0 °C

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Using gas–liquid chromatography, we obtained infinite-dilution partition and activity coefficients at 30.0 °C for *n*-pentane and six haloalkane solutes in pure squalane, in pure dinonyl phthalate, and in five mixtures thereof. Where appropriate the results are contrasted with those from previous studies. Partition coefficients were found to differ by as much as 10% from those calculated from the partition coefficients for the pure single solvents by using the Purnell–Andrade equation. Theoretical expressions derived by Harbison et al. fitted the data within experimental error and were used to calculate interaction parameters. The results indicated the existence of a weak 1:1 complex between each of the haloalkane solutes and dinonyl phthalate. The association constants of these complexes were evaluated and their trends were qualitatively interpreted.

Introduction

For a variety of gas–liquid chromatographic (GLC) systems in which a volatile solute component (A) is distributed between a binary nonvolatile solvent mixture (B + C) and the gas phase, Purnell and de Andrade (*1*) find that the linear relation

$$K^0_{R(M)} = \phi_B K^0_{R(B)} + \phi_C K^0_{R(C)} \qquad (1)$$

is obeyed within experimental error. $K^0_{R(B)}$ and $K^0_{R(C)}$ are the infinite-dilution solute partition coefficients in pure B and C, respectively. $K^0_{R(M)}$ is the infinite-dilution solute partition coefficient in a mixture where the volume fractions of B and C are ϕ_B and ϕ_C, respectively. On the other hand Harbison et al. (*2*) derive the expression

$$\ln K^0_{R(M)} = \phi_B \ln K^0_{R(B)} + \phi_C \ln K^0_{R(C)} + (\bar{V}_A/\bar{V}_B)\chi_{C(B)}\phi_B\phi_C \qquad (2)$$

which, in general, predicts curvature in plots of $K^0_{R(M)}$ vs. ϕ_C. $\bar{V}$ represents molar volumes, and $\chi_{C(B)}$ is the Flory-type interaction parameter characterizing B–C interactions.

While eq 1 (and extensions of it to solvents of up to five components (*3*)) has been used in the window diagram method (*3–5*) for optimizing chromatographic separations, several studies (*2*, *6–10*) have shown that it remains an approximate description of the true physical situation. In these studies nonlinear $K^0_{R(M)}$ vs. ϕ_C plots were obtained. In two of these studies (*2*, *10*) eq 2 fitted the results to within experimental error.

In this study infinite-dilution partition coefficients were obtained at 30.0 °C from GLC for *n*-pentane and six haloalkane solutes in squalane (SQ)–dinonyl phthalate (DNP) solvent mixtures. For all the solutes studied plots of $K^0_{R(M)}$ vs. ϕ_C were nonlinear. The results were analyzed and discussed in light of the treatment of Harbison et al. (*2*).

Experimental Section

Squalane (SQ) and di-*n*-nonyl phthalate (DNP) were used as received from Applied Science and Eastman, respectively. High-purity solutes were also used as received from standard suppliers. The stationary liquids and their mixtures were deposited on Chromosorb W (60/80 mesh, acid-washed and DMCS treated) solid support from solutions in methylene chloride. The methylene chloride was removed by rotary evaporation. Traces of methylene chloride were removed from the coated supports by placing them in a vacuum desiccator for several days. The free-flowing powders were then packed into previously coiled 1-m-long and 0.25-in.-o.d. stainless steel columns. The weight percent of the liquid phase employed was in the neighborhood of 10% and was determined from the weight loss of three separately ashed samples (ca. 1 g each) of coated support (*11*). Seven different columns were used at 30.0 °C with the following volume fractions of DNP (ϕ_C) in the solvent mixture: 0.000, 0.231, 0.410, 0.583, 0.671, 0.851, and 1.000. The solutes studied are listed in Table I.

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Table I. Properties of the Pure Components at 30.00 °C

	$\bar{V}$, cm^3 mol^{-1}	p^0_A, mmHg	$-B_{AA}$, cm^3 mol^{-1}
solutes			
n-pentane	117.03	614.80	1146
dichloromethane	64.99	529.97	803
trichloromethane	80.86	238.77	1142
bromochloromethane	67.70	183.40	1300
1,2-dichloroethane	79.91	99.82	1650
1-chlorobutane	105.75	128.06	1930
2-bromobutane	109.95	81.46	2400
solvents			
squalane (B)	526.54		
dinonyl phthalate	435.95		

Table I gives the molar volumes of the pure liquid components and the saturation vapor pressure and second virial coefficients of the solutes at 30.0 °C. The solute molar volumes and vapor pressures were obtained from Dreisbach's (*12*) compilation, while second virial coefficients were calculated from known critical constants (*12*) and a refined corresponding states relation (*13*, *14*). The molar volumes of SQ and DNP were determined from density measurements using an Anton Paar digital precision system (*15*) and were, respectively, 0.03% lower and 0.14% higher than those reported by Harbison et al. (*2*). Mixtures of SQ + DNP were found to have an effectively zero volume of mixing.

The gas chromatographic system used was largely of laboratory construction, and designed to achieve high precision in the measurement of partition coefficients. High-purity helium was passed through a tube packed with activated molecular sieve to remove any traces of moisture that may be present. The helium was then passed through the pressure regulator of a Beckman 2160 gas chromatograph and onto an injection port (thermostated at 170 °C during all runs) from a disused gas chromatograph. The columns were placed in a well-insulated and carefully thermostated water bath at 30.00 °C. The bath temperature was controlled to within +0.02 °C. Using a mercury manometer connected to the column inlet, we measured the inlet pressure to the nearest 0.5 mmHg. The column outlet was connected to the thermal conductivity detector (kept at 180 °C during all runs) on the Beckman 2160 gas chromatograph using $^1/_{16}$-in. tubing which was heated to avoid solute condensation. The pressure at the outlet of the column (barometric pressure) was regularly measured throughout the runs to better than 0.5 mmHg. The carrier gas flow rate was measured with a soap-bubble flow meter.

The details of the procedure followed to obtain precise partition coefficients have been described elsewhere (*11*, *16*). Sample size variation established the attainment of the infinite dilution condition (*16*, *17*). Varying solvent/support ratio indicated that interfacial effects were absent (*16*, *18*). The percent standard deviation in $K^0_{R(S)}$, calculated from the standard relation

$$K^0_{R(S)} = jF_c t_R'/V_S \tag{3}$$

was found (*11*) to be 1.2%. V_S is the volume of the stationary liquid in the column, j is the compressibility factor, F_c is the corrected flow rate, and t_R' is the retention time adjusted for column dead space ($t_R' = t_R - t_A$). Use of helium as carrier gas alongside relatively low inlet pressures made virial corrections unnecessary, and the measured partition coefficients, $K_{R(S)}$, correspond to those at zero column pressure drop, $K^0_{R(S)}$. In Table II K^0_R values as functions of the volume fraction of DNP are given.

Results and Discussion

The solute (A) partition coefficient with pure SQ (B) and pure DNP (C) were converted to fully corrected activity coefficients $\gamma_{A(B)}$ (or $\gamma_{A(C)}$) via the relation

$$\gamma_{A(B)} = \frac{RT}{\bar{V}_B p^0_A K^0_{R(B)}} \exp\left\{\frac{-(B_{AA} - \bar{V}_A)p^0_A}{RT}\right\} \tag{4}$$

p^0_A and B_{AA} are the bulk solute vapor pressure and virial coefficient, T is the column temperature, and $\bar{V}_B$ (or $\bar{V}_C$) is the molar volume of the stationary phase. As Tables III and IV and Figure 1a show the results for *n*-pentane are in excellent agreement with recent careful measurements (*2*, *7*, *19*). Except for the static measurements of Freeguard and Stock (*20*), the results for dichloromethane, trichloromethane, and 1,2-dichloroethane, given in Table III, are in reasonable agreement with those from earlier studies (*20*, *21*).

Table II. Partition Coefficients as Functions of Volume Fractions at 30.00 °C

	ϕ_{DNP}						
solute	0.000	0.231	0.410	0.583	0.671	0.851	1.000
n-pentane	98.53	93.30	90.00	83.25	78.75	72.49	65.92
dichloromethane	77.08	121.7	157.1	184.1	195.8	222.2	244.8
trichloromethane	225.8	358.0	463.4	540.2	570.5	637.1	690.3
bromochloromethane	201.4	313.0	405.7	476.6	504.4	575.4	630.8
1,2-dichloromethane	285.3	444.2	573.1	679.6	721.3	822.2	909.3
1-chlorobutane	373.8	448.1	503.7	535.1	537.0	548.2	568.6
2-bromobutane	581.6	705.1	796.8	843.3	849.9	876.0	902.4

Table III. Infinite-Dilution Solute Activity Coefficients with Pure Squalane and with Pure Dinonyl Phthalate Solvents at 30.00 °C from GLC (G) and Static (S) Studies

	$\gamma^\infty_{A(B)}$ (SQ)			$\gamma^\infty_{A(C)}$ (DNP)		
solute	this study	other studies	% diff[a]	this study	other studies	% diff[a]
n-pentane	0.618	0.617 (G)[b]	+0.2	1.115	1.117 (G)[b]	−0.2
		0.620 (S)[c]	−0.3		1.115 (S)[c]	0.0
dichloromethane	0.901	1.076 (S)[d]	−16.3	0.334	0.379 (S)[d]	−11.9
		0.904 (G)[e]	−0.3		0.329 (G)[e]	−1.5
trichloromethane	0.676	0.653 (S)[d]	+3.5	0.267	0.251 (S)[d]	+6.4
		0.647 (G)[e]	+4.5		0.257 (G)[e]	+3.9
bromochloromethane	0.985			0.380		
1,2-dichloroethane	1.273	1.230 (G)[e]	+3.5	0.482	0.450 (G)[e]	+7.1
		1.299 (S)[e]	−2.0		0.466 (S)[e]	+3.4
1-chlorobutane	0.760			0.604		
2-bromobutane	0.766			0.596		

[a] Relative to the other study. [b] Reference 2. [c] Reference 19. [d] Reference 20. [e] Reference 21.

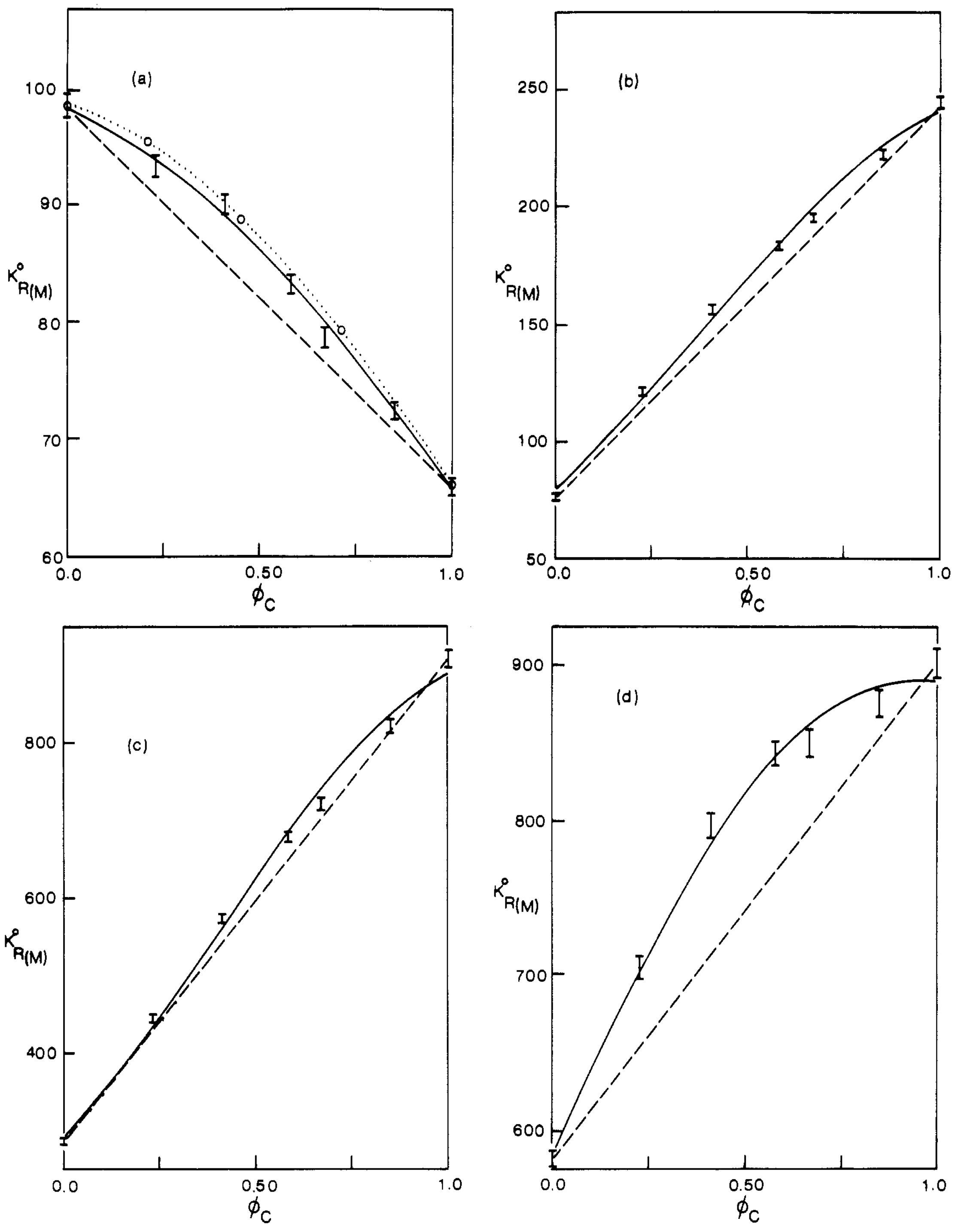

Figure 1. Partition coefficients as a function of volume fraction of dinonyl phthalate in squalane at 30.00 °C for (a) *n*-pentane, (b) dichloromethane, (c) 1,2-dichloroethane, and (d) 2-bromobutane. Points with 1.2% error bars are experimental points; circles and dotted line in (a) are at 303 K and taken from ref *7* and *19*; solid curves using eq 16 of ref 2; dashed line, using eq 1.

Table IV. Infinite-Dilution Activity Coefficients of *n*-Pentane with Mixtures of Squalane and Dinonyl Phthalate Solvents at 30.00 °C (This Study) and 303 K (Other Studies)

ϕ_C	this study	other studies
0.000	0.618	0.620[a]
0.216	0.669	0.669[b]
0.453	0.752	0.753[b]
0.713	0.888	0.887[b]
1.000	1.115	1.115[a]

[a] Reference 19. [b] Reference 7.

Table V. Interaction Parameters at 30.00 °C

solute	$\chi_{A(B)}$	$\chi_{A(C)}$	$\chi_{C(B)}$	% fit
n-pentane	0.244	0.702	1.069	0.622
n-pentane[a]	0.246	0.702	1.001	0.60
n-pentane[b]	0.245	0.698	1.143	
dichloromethane	1.111	0.058	5.734	1.8
trichloromethane	0.636	−0.408	5.215	1.8
bromochloromethane	1.165	0.085	5.489	1.4
1,2-dichloroethane	1.278	0.187	4.530	1.4
1-chlorobutane	0.532	0.175	1.939	0.88
2-bromobutane	0.509	0.133	1.941	0.82

[a] Reference 2. [b] Reference 7.

Plots of $K^0_{R(M)}$ vs. ϕ_C are presented for *n*-pentane (Figure 1a) and for representative haloalkane solutes (Figure 1b–d). The curvature and asymmetry of the plots are similar to those previously encountered (*2*, *10*). They clearly show that the infinite-dilution partition coefficients for all the solutes examined

Table VI. Best-Fit Interaction Parameters and Association Constants for Haloalkane Solutes at 30.00 °C

solute	$\chi_{A(B)}$	$\chi'_{A(C)}$	K_{AC}, L mol^{-1}	% fit
dichloromethane	1.102	1.188	1.01 ± 0.12	0.78
trichloromethane	0.636	0.851	1.15 ± 0.12	0.70
bromochloromethane	1.165	1.265	1.02 ± 0.11	0.58
1,2-dichloroethane	1.270	1.325	0.96 ± 0.10	0.57
1-chlorobutane	0.531	0.852	0.43 ± 0.06	0.81
2-bromobutane	0.507	0.822	0.44 ± 0.05	0.68

in this study deviate from the values calculated by using eq 1 and agree, within experimental error, with values calculated from eq 2 which allows for interaction between the two solvents.

Presented in Table V are the interaction parameters in pure SQ, pure DNP, and mixed solvent for each solute, evaluated by using eq 16 of ref *2*. The values for *n*-pentane are in good agreement with those from earlier studies (*2*, *7*). $\chi_{A(B)}$ and $\chi_{A(C)}$ for all the haloalkanes are generally higher and lower, respectively, than those for *n*-pentane. In addition $\chi_{C(B)}$ values which, according to the model of Harbison et al. (*2*), should be independent of the nature of the solute are appreciably larger for haloalkane solutes than for *n*-pentane. These seemingly anomalous results have been previously encountered (*2*, *10*). They are rationalized on the basis of a 1:1 A–C "complex" between each of the haloalkane solutes and DNP. From a least-squares analysis of the haloalkane data according to eq 19 of ref 2, K_{AC} the association constant of a weak A–C complex and $\chi'_{A(C)}$ the parameter characterizing solute–solvent interactions in the absence of complex formation were obtained. The results are given in Table VI.

The $\chi'_{A(C)}$ and $\chi_{A(B)}$ values in Table VI compare more reasonably with each other than the $\chi_{A(C)}$ and $\chi_{A(B)}$ values in Table V, indicating weak complexation between the haloalkane solutes and DNP. K_{AC} is about 0.4 for the monohaloalkanes and about 1.0 for the dihaloalkanes. Contrasting the results for dichloromethane and trichloromethane shows that the extra chlorine atom in the latter molecule has little effect, if any, on the K_{AC} value, possibly due to a steric hindrance. The closeness of the results for dichloromethane and bromochloromethane on one hand and 1-chlorobutane and 2-bromobutane on the other indicates that the chlorine and bromine atoms contribute nearly equally to the value of K_{AC}, possibly because of large separations between weakly "complexing" molecules.

Finally Table VII presents experimental and calculated (using eq 1) values of $K^0_{R(M)}$ for all the haloalkane solutes used in this study at $\phi_C = 0.453$ ($x_C = 0.500$). Large deviations (up to 10%) from linearity as prescribed by eq 1 exist at this mole fraction. In addition the two sets of relative (1-chlorobutane = 1.000) partition coefficients (α's) are different, with the difference reaching 4.6% in the case of 1,2-dichloroethane. Such large variations in α can affect the degree of success achieved by predictions, made on the basis of eq 1, of relative data for mixed solvents of comparable volume fractions.

Conclusion

Partition coefficients for *n*-pentane and six haloalkane solutes at infinite dilution in SQ–DNP mixtures differ from the values calculated by the Purnell–Andrade equation by as much as 10% and agree, to within experimental error, with an equation derived by Harbison et al. (*2*) on the basis of conventional models of solution. Clearly the systems examined in this study conform more to conventional theory of liquid mixtures than to a "micropartitioning" theory.

Table VII. Relative Partition Coefficients (α Values) at $\phi_C = 0.453$ (1-Chlorobutane = 1.000)

solute	eq 1[a]		exptl		% diff[b]	
	$K^0_{R(M)}$	α	$K^0_{R(M)}$	α	$K^0_{R(M)}$	α
dichloromethane	153.1	0.331	161.7	0.319	5.6	−3.6
bromochloromethane	395.6	0.857	418.0	0.826	5.7	−3.6
trichloromethane	436.2	0.944	478.3	0.945	9.7	+0.1
1-chlorobutane	462.0	1.000	506.3	1.000	9.6	
1,2-dichloroethane	568.0	1.229	593.7	1.173	4.5	−4.6
2-bromobutane	726.9	1.573	799.6	1.579	10.0	+0.4

[a] Using experimental end points ($K^0_{R(B)}$ and $K^0_{R(C)}$) at $\phi_{DNP} = 0.000$ and $\phi_{DNP} = 1.000$ in Table II. [b] Between the value obtained by using eq 1 and the experimental value.

The various solute–solvent and solvent–solvent interaction parameters were calculated on the basis of the treatment of Harbison et al. (*2*). The results indicated the formation of a weak 1:1 complex between each of the haloalkane solutes and DNP. Association constants were evaluated and qualitatively rationalized on the basis of the structures of the haloalkane molecules.

Registry No. SQ, 111-01-3; DNP, 84-76-4; pentane, 109-66-0; dichloromethane, 75-09-2; trichloromethane, 67-66-3; bromochloromethane, 74-97-5; 1,2-dichloroethane, 107-06-2; 1-chlorobutane, 109-69-3; 2-bromobutane, 78-76-2.

Literature Cited

(1) Purnell, J. H.; Vargas de Andrade, J. M. *J. Am. Chem. Soc.* **1975**, *97*, 3585–3592.

(2) Harbison, M. W. P.; Laub, R. J.; Martire, D. E.; Purnell, J. H.; Williams, P. S. *J. Phys. Chem.* **1979**, *83*, 1262–1268 and references therein.

(3) Laub, R. J.; Purnell, J. H.; Williams, P. S. *Anal. Chim. Acta* **1977**, *95*, 135–142.

(4) Laub, R. J.; Purnell, J. H.; Williams, P. S. *J. Chromatogr.* **1977**, *134*, 249–261.

(5) Laub, R. J.; Purnell, J. H.; Summers, D. M.; Williams, P. S. *J. Chromatogr.* **1978**, *155*, 1–8.

(6) Ashworth, A. J.; Hooker, D. M. *J. Chromatogr.* **1977**, *131*, 399–403.

(7) Ashworth, A. J.; Hooker, D. M. *J. Chromatogr.* **1979**, *174*, 307–313.

(8) Ashworth, A. J.; Price, G. J. *J. Chromatogr.* **1982**, *238*, 89–95.

(9) Ashworth, A. J.; Letcher, T. M.; Price, G. J. *J. Chromatogr.* **1983**, *262*, 33–39.

(10) Meyer, E. F.; Meyer, A. J. *J. Phys. Chem.* **1981**, *85*, 94–97.

(11) Laub, R. J.; Purnell, J. H.; Williams, P. S.; Harbison, M. W. P.; Martire, D. E. *J. Chromatogr.* **1978**, *155*, 233–240.

(12) Dreisbach, R. R. "Physical Properties of Chemical Compounds"; American Chemical Society: Washington, D. C., 1959; Vol. II.

(13) McGlashan, M. L.; Potter, D. J. B. *Proc. R. Soc. London, Ser. A* **1962**, *267*, 478–484.

(14) Guggenheim, E. A.; Wormald, C. J. *J. Chem. Phys.* **1965**, *42*, 3775–3780.

(15) Oweimreen, G. A.; Hassan, M. *Mol. Cryst. Liq. Cryst.* **1983**, *100*, 351–371.

(16) Oweimreen, G. A.; Lin, G. C.; Martire, D. E. *J. Phys. Chem.* **1979**, *83*, 2111–2119.

(17) Martire, D. E.; Riedl, P. *J. Phys. Chem.* **1968**, *72*, 3478–3488.

(18) Liao, H. L.; Martire, D. E. *Anal. Chem.* **1972**, *44*, 498–502.

(19) Ashworth, A. J. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 459–466.

(20) Freeguard, G. F.; Stock, R. S. *Trans. Faraday Soc.* **1963**, *59*, 1655–1662.

(21) Sewell, P. A.; Stock, R. S. *J. Chromatogr.* **1970**, *50*, 10–16.

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