TABLE 2
Hildebrand Parameters from Experimental Vaporization Enthalpies

Liquid	δ/MPa$^{1/2}$ 25°C	Normal boiling point (°C)
Aliphatic hydrocarbons		
Pentane	14.5	14.1 (36.0)
Isopentane, 2-methylbutane	13.9	13.9 (27.9)
Hexane	14.9	13.8 (68.7)
2-Methylpentane	14.4	13.5 (60.3)
3-Methylpentane	14.6	13.6 (63.3)
2,2-Dimethylbutane	13.8	12.2 (49.7)
2,3-Dimethylbutane	14.4	13.5 (58.0)
Heptane	15.2	13.4 (98.4)
2-Methylhexane	14.8	13.2 (90.1)
3-Methylhexane	15.1	13.4 (91.9)
2,2,3-Trimethylbutane	14.4	13.1 (80.9)
2,3-Dimethylpentane	15.2	13.6 (89.8)
Octane	15.5	13.0 (125.6)
2-Methylheptane	15.3	13.0 (117.7)
4-Methylheptane	15.3	13.0 (117.7)
Isooctane, 2,2,4-trimethylpentane	14.1	12.4 (99.2)
1-Octene	15.5	13.2 (121.3)
Alicyclic hydrocarbons		
Cyclopentane	17.0	16.3 (49.3)
Cyclohexane	16.6	15.2 (80.7)
Methylcyclopentane	16.1	14.9 (71.8)
Methylcyclohexane	16.0	14.3 (100.9)
cis-1,3-Dimethylcyclopentane	16.0	14.3 (90.8)
Ethylcyclohexane	16.3	13.8 (131.8)
Aromatic hydrocarbons		
Benzene	18.7	17.1 (80.1)
Toluene, methylbenzene	18.2	16.1 (110.6)
Ethylbenzene	18.0	15.2 (136.2)
o-Xylene, *o*-dimethylbenzene	18.3	15.5 (144.4)
m-Xylene, *m*-dimethylbenzene	18.1	15.4 (139.1)
p-Xylene, *p*-dimethylbenzene	18.0	15.3 (138.4)
Ethers		
Diethyl ether	15.5	15.2 (34.5)
Dipropyl ether	15.6	13.8 (90.0)
Diisopropyl ether	14.5	13.3 (68.3)
Dibutyl ether	15.8	13.0 (140.3)
Methyl propyl ether	15.8	15.4 (39.0)
Methyl isopropyl ether	15.5	15.2 (32.5)
Methyl butyl ether	15.9	14.6 (70.2)
Ethyl propyl ether	15.5	14.4 (63.1)
Ethyl isopropyl ether	15.3	14.4 (54.0)
Ethyl butyl ether	15.7	13.9 (92.3)

TABLE 2 (continued)
Hildebrand Parameters from Experimental Vaporization Enthalpies

Liquid	δ/MPa$^{1/2}$ 25°C	Normal boiling point (°C)
Esters		
Ethyl formate	19.2	18.1 (54.3)
Propyl formate	19.0	17.2 (80.9)
Butyl formate	18.3	15.9 (105.6)
Methyl acetate	19.4	18.3 (56.9)
Ethyl acetate	18.4	16.7 (77.2)
Propyl acetate	18.0	15.6 (101.6)
Butyl acetate	17.8	14.8 (126.1)
Methyl propionate	18.6	16.9 (79.8)
Ethyl propionate	17.9	15.6 (99.1)
Propyl propionate	17.6	14.8 (122.4)
Amines		
Propylamine	18.8	17.9 (47.3)
Butylamine	18.4	16.7 (77.1)
Isobutylamine	17.8	16.3 (67.5)
sec-Butylamine	17.3	16.0 (62.7)
Diethylamine	17.0	16.0 (55.6)
Diisopropylamine	14.7	12.3 (83.6)
N-Methylisopropylamine	16.5	15.6 (50.4)
N-Ethylisopropylamine	15.9	14.5 (69.7)
N-Propylisopropylamine	16.3	14.2 (96.9)
N-Butylisopropylamine	15.9	13.3 (123.4)
N-Ethylbutylamine	16.6	14.2 (107.5)
Cyclohexylamine	18.9	16.0 (134.0)
Triethylamine	15.2	13.7 (88.9)
Chlorinated hydrocarbons		
Dichloromethane, methylene dichloride	20.3	19.8 (40.0)
Trichloromethane, chloroform	18.9	17.8 (61.2)
Tetrachloromethane, carbon tetrachloride	17.6	16.2 (76.7)
1,2-Dichloroethane, ethylene dichloride	20.3	18.5 (83.5)
1,1,1-Trichloroethane, methyl chloroform	17.3	16.0 (74.0)
1,1,2-Trichloroethane	20.1	17.4 (113.5)
1,1,2,2-Tetrachloroethane	20.2	16.9 (146.1)
Trichloroethylene	18.9	17.2 (87.3)
Tetrachloroethylene	19.0	16.6 (121.0)
Aldehyde		
Propanal, propionaldehyde	19.4	18.5 (48.8)
Ketones		
Acetone, 2-propanone	19.7	18.6 (56.2)
Methyl ethyl ketone, 2-butanone	19.0	17.2 (79.6)
Methyl propyl ketone, 2-pentanone	18.2	16.1 (102.4)
Diethyl ketone, 3-pentanone	18.4	16.2 (102.0)
Ethyl butyl ketone, 3-hexanone	17.9	15.2 (123.5)
3-Methyl-2-butanone	17.8	15.8 (94.4)

TABLE 2 (continued)
Hildebrand Parameters from Experimental Vaporization Enthalpies

Liquid	δ/MPa$^{1/2}$ 25°C	Normal boiling point (°C)
Alcohols		
Methanol	30.5	29.1 (64.8)
Ethanol	26.5	24.2 (78.3)
2-Propanol, isopropanol	23.9	21.4 (82.2)
1-Butanol	23.8	20.1 (117.8)
1-Pentanol, amyl alcohol	22.5	18.3 (138.1)
Isobutanol, 2-methyl-1-propanol	22.9	19.7 (108.0)

Data selected and adapted from Wágner, Z., Majer, V., and Svoboda, V., *Chem. Listy*, 77, 1150, 1983.

$$\mathrm{d}\ \ln p/\mathrm{d}T = \Delta H_{ap}/(RT^2) \tag{7}$$

which defines the apparent molar enthalpy of vaporization, ΔH_{ap}. It follows that

$$\Delta H = \Delta H_{ap}\left(\frac{p\Delta V}{\mathrm{RT}}\right) = \Delta H_{ap}\, Z\left(\frac{{}^{g}V - V}{{}^{g}V}\right) \tag{8}$$

where $Z = p\,{}^{g}V/(RT)$ is the compressibility factor, which is unity for an ideal gas but less than unity for real gases. Consequently,

$$\Delta U = \Delta H - p\,\Delta V = \Delta H_{ap}\, Z\left(\frac{{}^{g}V - V}{{}^{g}V}\right) - p({}^{g}V - V) = Z(\Delta H_{ap} - RT) \tag{9}$$

and

$$\delta = [(\Delta H_{ap} - RT)Z/V]^{1/2} \tag{10}$$

This equation reduces to the original definition (Equation 6, Chapter 2) for $Z = 1$. It was used in this form by Sunwoo and Eisen[22] for solvents of pharmaecutical interest. Polak[21] used the alternative nonideality correction coefficient

$$B = {}^{g}V - RT/p \tag{11}$$

in calculating the cohesion energies previously presented (Table 1, Chapter 2).

Several empirical and semiempirical equations have been used for the evaluation of vaporization energies and cohesion parameters of liquids.[20,23-27] In particular, Hoy (Union Carbide Corporation)[26,27] used semiempirical relations in the estimation of Hildebrand parameters and Hansen parameters (Section 5.11) for the wide range of liquids (and solids as subcooled liquids) listed in Table 18, Chapter 5. The Haggenmacher[28] equations are

$$p({}^{g}v - v) = \frac{RT}{M}\left(1 - \frac{pT_c^3}{p_cT^3}\right)^{1/2} \tag{12}$$

$$\Delta H = \frac{dp}{\mathrm{dT}}\frac{RT^2}{Mp}\left(1 - \frac{pT_c^3}{p_cT^3}\right)^{1/2} \tag{13}$$