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Ultrasonic Velocity, Density, and Adiabatic Compressibility for 2,6-Dimethylpyridine + Water in the Temperature Range 293−318 K

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Ultrasonic velocities and densities for 2,6-dimethylpyridine (1) + water (2) were measured over the entire composition range in the temperature interval 293−318 K. Using the Laplace formula, the adiabatic compressibility was calculated. The results and the empirical smoothing polynomials are presented. The density decreases monotonically with an increase of the amine concentration, while the velocity and compressibility isotherms show two points of interest: a nearly common crossing point at a mole fraction $x_1 \approx 0.03$ and extrema at $x_1 \approx 0.15$.

Introduction

The 2,6-dimethylpyridine (1) + water (2) system shows a closed miscibility gap. According to Andon and Cox (1952), the lower and upper consolute temperatures are $t = 34.0 \pm 0.2$ °C (mole fraction $x_1 = 0.067$) and $t = 230.7 \pm 1$ °C ($x_1 = 0.105$), respectively. This finding has been confirmed by other researchers who reported consolute points very close to those given by Andon and Cox (1952).

Although this binary system has been extensively investigated, to the best of our knowledge, the only paper devoted to its ultrasonic properties is that of Gutschick and Pings (1971) in that the ultrasound absorption and velocity in the vicinity of the lower critical mixing point ($t_c \pm 1$ °C) were given graphically; the adiabatic compressibility has not been calculated. On the contrary, the densities of 2,6-dimethylpyridine + water are available in the literature (e.g., Abe et al. (1978), Grattoni et al. (1993), and Jayalakshmi et al. (1994)) but only for a rather narrow temperature interval. Furthermore, the density data are rather inconsistent, most probably because of different extents of contamination of the samples studied by 3- and 4-methylpyridine and water that are usually present in commercial 2,6-dimethylpyridine. Since this work was aimed mainly at the compressibility of 2,6-dimethylpyridine + water, both the ultrasonic velocities and densities were measured in order to obtain consistent data.

We present data for a rather wide temperature range covering the single-phase system far below (ca. 15 °C) and above (ca. 10 °C) the lower consolute point, while the majority of the studies were focused on the properties of critical mixtures of 2,6-dimethylpiridine and water in the neighborhood of this point.

Experimental Section

Chemicals. 2,6-Dimethylpyridine of purity 99+% was supplied by Aldrich and used without further purification. The comparison of experimental and literature densities and refractive indices is given in Table 1. The mass fraction of water in the amine, determined by the Karl Fischer method, was 0.028%. 2,6-Dimethylpyridine is flammable, hygroscopic, and toxic and is an irritant; it should be stored and handled under nitrogen.

Solutions were prepared by mass, using degassed redistilled water with electrolytic conductivity 1.5×10^{-4} S m^{-1}, and stored under nitrogen in sealed flasks. The gas bubbles, formed during mixing of the critical solutions, were removed in an ultrasonic cleaner (Unitra-Unima UM-4, $f \approx 25$ kHz, electric power ≥40 W). As indicated by the refractive indices measured before and after 40 min of the ultrasonic treatment, this procedure did not cause any change in the mixture compositions. In the calculation of solution concentrations the correction for water content in 2,6-dimethylpyridine was applied. The random error in mole fraction, resulting from the errors in weighing and Karl Fischer titration, varies from $\pm 0.3 \times 10^{-4}$ at $x_1 \approx 0.01$ to $\pm 1 \times 10^{-4}$ at $x_1 \approx 1$.

Table 1. Density and Refractive Index of 2,6-Dimethylpyridine Used in the Experiment

	ρ/(kg m^{-3})	
t/°C	exptl	lit.
20	922.56	922.57[a]
22	920.78	921.3[b]
25	918.11	918.06,[a] 918.3,[c] 918.45[d]
30	913.63	913.55[a]
33.5	910.48	910.970[e]

	n_D	
t/°C	exptl	lit.
20	1.4970 ± 0.0002	1.4971,[c] 1.49767[a]

[a] Biddiscombe, D. P.; Coulson, E. A.; Handley, R.; Herington, E. F. G. *J. Chem. Soc.* **1954**, 1957, cited by Abe et al. (1978) (25 °C) and by Timmermans (1965) (20 and 30 °C). [b] Grattoni et al. (1993) (accuracy ±0.1 kg m^{-3}). [c] Brown H. C.; Johnson S.; Podall H. *J. Am. Chem. Soc.* **1954**, *76*, 5556, cited by Timmermans (1965). [d] Abe et al. (1978). [e] Jayalakshmi et al. (1994) (relative accuracy 2×10^{-3} kg m^{-3}, absolute accuracy 10^{-1} kg m^{-3}).

Ultrasonic Velocity and Density Measurements. The ultrasonic group velocity at $f \approx 4$ MHz was measured by the sing-around technique (see e.g. Hall and Yeager (1973)) using a velocimeter designed and constructed in our laboratory (electronic part) and at the Institute of Fundamental Technological Research of the Polish Academy of Sciences, Warsaw (sample cell). Deionized water with an electrolytic conductivity of 0.6×10^{-4} S m^{-1} was used as a standard for calibration. The pulse transit time (τ) in the electroacoustic loop was measured for 15 temperatures differing by about 2 K within the interval 291−319 K. The speeds of sound in water (u) calculated from the polynomial of Del Grosso and Mader (1972) were taken as true values. The apparatus constants were calculated by the least squares fit to the following equation:

$$\tau = l_0(1 + \alpha\Delta T)/u + \tau_{el} \qquad (1)$$

where $l_0 \approx 5$ cm is the acoustic path length at $T_0 = 293.15$

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Table 2. Densities of 2,6-Dimethylpyridine (1) + Water (2) Measured with a Bicapillary Pycnometer[a]

x_1	t/°C	ρ/(kg m^{-3})	t/°C	ρ/(kg m^{-3})	t/°C	ρ/(kg m^{-3})	t/°C	ρ/(kg m^{-3})	t/°C	ρ/(kg m^{-3})	t/°C	ρ/(kg m^{-3})	t/°C	ρ/(kg m^{-3})	t/°C	ρ/(kg m^{-3})	t/°C	ρ/(kg m^{-3})
0.012 66	19.98	998.015			24.99	996.346			29.98	994.644			34.98	992.720	39.98	990.584	44.98	988.073
0.015 02	19.98	997.876			24.98	996.265			29.98	994.511			34.99	992.543	39.99	990.219	44.99	987.890
0.026 96	19.98	997.763			24.99	995.780			29.98	993.636			34.97	991.210				
0.049 95	19.97	997.208	22.49	995.934	24.99	994.588	27.48	993.244	29.96	991.858	31.99	990.681						
0.069 91	19.98	996.634	22.49	995.132	24.99	993.573	27.48	991.996	29.98	990.414	31.98	989.096						
0.099 99	19.98	995.579	22.49	993.779	24.98	991.980	27.47	990.167	29.97	988.329	32.47	986.441						
0.139 88	20.01	993.793			24.98	989.768			29.97	985.657			34.98	981.471				
0.259 24	19.98	986.077			24.97	981.416			29.97	976.751			34.99	971.977	39.98	967.181	44.99	962.278
0.399 31	19.97	974.010			25.00	969.176			29.97	964.419			34.98	959.537	39.98	954.595	44.98	949.578
0.598 91	19.97	955.273			24.99	950.534			29.98	945.792			34.97	940.986	39.98	936.018	44.99	931.201
0.798 32	19.99	937.377			24.99	932.771			29.98	928.211			34.98	923.622	39.99	918.933	44.97	914.207
0.998 30	19.98	922.695			24.98	918.208			29.99	913.727			34.98	909.272	39.98	904.726	44.98	900.135

[a] The lack of some data at $t > 34$ °C results from the phase separation of the system.

Table 3. Ultrasonic Group Velocity at $f \approx 4$ MHz in 2,6-Dimethylpyridine (1) + Water (2) Measured with a Sing-Around Velocimeter[a]

x_1	t/°C	u/(m s^{-1})	t/°C	u/(m s^{-1})	t/°C	u/(m s^{-1})	t/°C	u/(m s^{-1})	t/°C	u/(m s^{-1})	t/°C	u/(m s^{-1})	t/°C	u/(m s^{-1})	t/°C	u/(m s^{-1})	t/°C	u/(m s^{-1})
0.012 66	20.16	1526.11			25.24	1535.41			29.70	1542.25			34.77	1548.55	39.89	1553.55	44.93	1557.03
0.015 02	20.17	1530.99			25.25	1539.40			29.68	1545.49			34.74	1551.03	39.82	1555.16	44.87	1557.54
0.026 96	20.20	1550.08			25.26	1554.31			29.69	1556.76			34.75	1557.93				
0.049 95	20.19	1573.14	22.22	1572.31	25.25	1570.59	27.27	1569.10	29.69	1566.90	31.74	1564.57						
0.069 91	20.23	1586.54	22.26	1583.99	25.29	1579.68	27.30	1576.46	29.70	1572.27	31.72	1568.28						
0.099 99	20.23	1600.71	22.26	1596.29	25.29	1589.29	27.30	1584.44	29.68	1578.36	31.71	1572.87						
0.139 88	20.19	1610.04			25.25	1595.03			29.70	1581.21			34.77	1564.68				
0.259 24	20.25	1598.92			25.30	1579.65			29.70	1562.59			34.73	1542.94	39.78	1522.98	44.77	1502.89
0.399 31	20.28	1560.85			25.26	1539.85			29.67	1521.37			34.72	1500.21	39.79	1478.86	44.82	1457.66
0.598 91	20.22	1496.26			25.25	1474.60			29.66	1455.60			34.71	1434.01	39.80	1412.24	44.84	1390.76
0.798 32	20.24	1431.38			25.27	1410.22			29.67	1391.72			34.68	1370.79	39.76	1349.67	44.78	1328.90
0.998 30	20.15	1381.67			25.24	1360.38			29.68	1341.94			34.75	1321.02	39.86	1300.22	44.94	1279.91

[a] The lack of some data at $t > 34$ °C results from the phase separation of the system.

Table 4. Coefficients of the Density and Ultrasound Velocity Polynomials (3) for 2,6-Dimethylpyridine (1) + Water (2) for 293 K < *T* < T_{max} and Mean Deviations from the Regression Lines δ_ρ and δ_u

x_1	ρ_0/(kg m^{-3})	ρ_1/(kg m^{-3} K^{-1})	ρ_2/(kg m^{-3} K^{-2})	δ_ρ/(kg m^{-3})	u_0/(m s^{-1})	u_1/(m s^{-1} K^{-1})	u_2/(m s^{-1} K^{-2})	δ_u/(m s^{-1})	T_{max}/K
0.012 66	1002.004	−0.1169	−0.004 26	0.07	1475.024	3.1152	−0.028 72	0.07	318
0.015 02	1002.090	−0.1274	−0.004 20	0.05	1482.360	3.0095	−0.029 71	0.05	318
0.026 96	1003.325	−0.1887	−0.004 50	0.03	1516.786	2.2910	−0.031 85	0.04	308
0.049 95	1006.019	−0.3773	−0.003 19	0.01	1563.924	1.2130	−0.037 54	0.05	305
0.069 91	1007.649	−0.5031	−0.002 40	0.01	1594.956	0.3283	−0.036 84	0.04	305
0.099 99	1009.043	−0.6399	−0.001 72	0.01	1632.166	−1.0045	−0.027 27	0.04	305
0.139 88	1009.354	−0.7521	−0.001 28	0.00	1661.475	−2.2180	−0.016 34	0.04	308
0.259 24	1003.954	−0.8712	−0.001 22	0.02	1673.769	−3.5975	−0.004 88	0.03	318
0.399 31	992.383	−0.8967	−0.001 22	0.02	1646.054	−4.2024	0	0.04	318
0.598 91	973.679	−0.9027	−0.000 94	0.05	1584.080	−4.3690	0.001 30	0.02	318
0.798 32	955.097	−0.8708	−0.000 85	0.03	1517.677	−4.3023	0.001 94	0.01	318
0.998 30	940.152	−0.8628	−0.000 59	0.03	1468.551	−4.4005	0.004 49	0.06	318
1[a]	940.060	−0.8630	−0.000 60		1468.286	−4.4049	0.004 56		318

[a] Extrapolated.

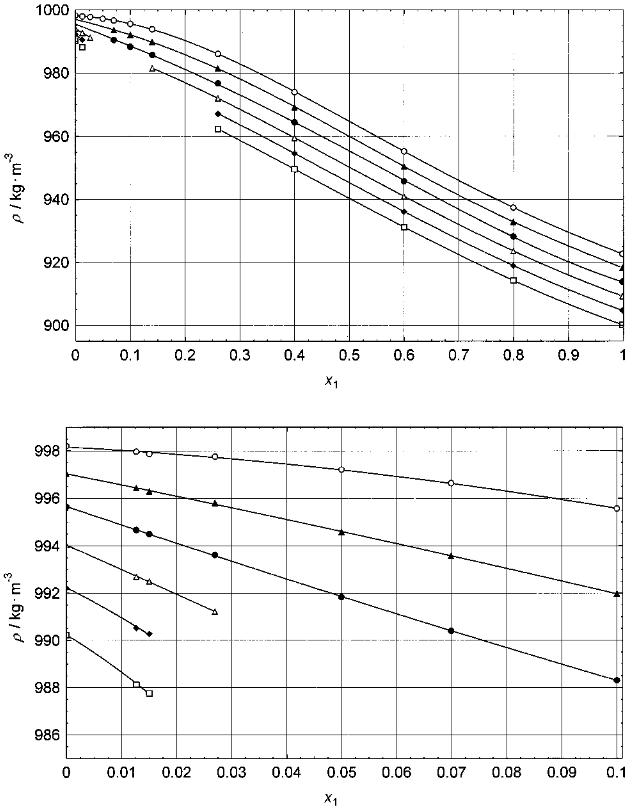

Figure 1. Density isotherms for 2,6-dimethylpyridine (1) + water (2): ○, 293.15 K; ▲, 298.15 K; ●, 303.15 K; △, 308.15 K; ◆, 313.15 K; □, 318.15 K; (top) in the whole concentration range (some points were omitted for clarity); (bottom) in dilute aqueous solutions. The phase separation of 2,6-dimethylpyridine + water at *t* > 34 °C causes some isotherms to be broken.

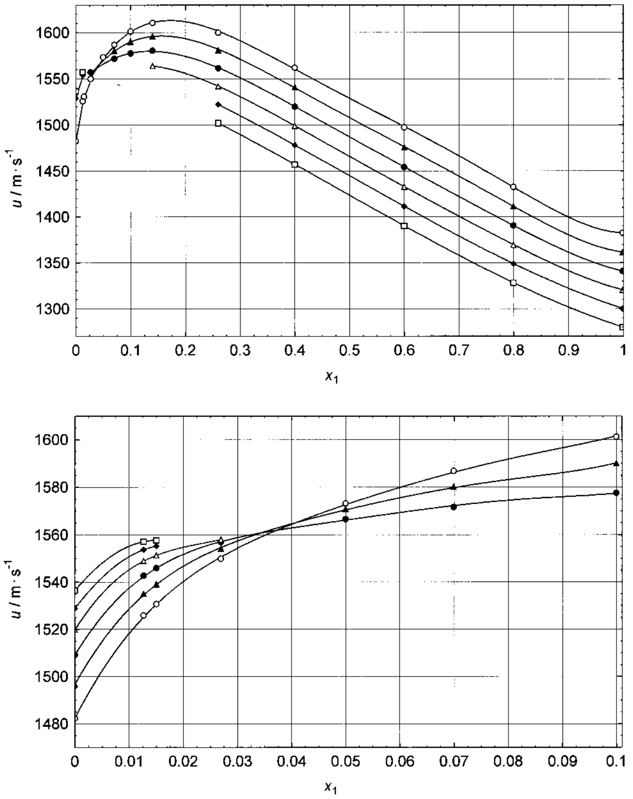

Figure 2. Ultrasonic velocity isotherms for 2,6-dimethylpyridine (1) + water (2): symbols as in Figure 1. (top) in the whole concentration range (some points were omitted for clarity), (bottom) in dilute aqueous solutions. The phase separation of 2,6-dimethylpyridine + water at *t* > 34 °C causes some isotherms to be broken.

K, α is the coefficient of the thermal expansion of the measuring cell, τ_{el} is the total electronic delay time (i.e., the time of the transmission of the pulse beyond the liquid under investigation), and $\Delta T = T - T_0$. The temperature of the sample was kept constant by a 15 dm^3 water bath controlled by a proportional-integrating temperature controller, Unipan 660, with an adjustable proportional band, integrating time, and heating power. The cooling water was supplied by another thermostat. Although the temperature fluctuations in the sample cell measured by a quartz thermometer with a resolution of 1×10^{-3} K did not exceed ±0.002 K in a 10 min period of measurement, the actual temperature gradients in the liquid being tested can reach ±0.01 K as we discussed earlier (Ernst et al., 1993). The precision of the speed of sound measurements depended on the difference between the measured velocity and that in the standard liquid (water) and varied from 0.05 to 0.30 m s^{-1} (confidence level 95%); the resolution equals 0.05 m s^{-1}. The accuracy can be estimated to be ±0.5 m s^{-1}; however, a reliable method for the calculation of the accuracy of sing-around velocimeters has not yet been worked out. The details concerning the measurement precision and testing of the velocimeter can be found in our work (Ernst et al., 1992), where a similar apparatus employing the first echo (i.e., the pulse traveling 3 times the distance between the transducers) was described. In the velocimeter used in this study, the subsequent pulse is generated by a pulse that travels only once throughout the acoustic path.

The densities of the solutions were measured with a 25 cm^3 bicapillary pycnometer. The liquid level in each capillary (ca. 10 cm in length and 0.1 cm in i.d.) was determined using a vertical cathetometer. The pycnometer was calibrated using the same water as applied for the velocimeter calibration. The density of water was calcu-

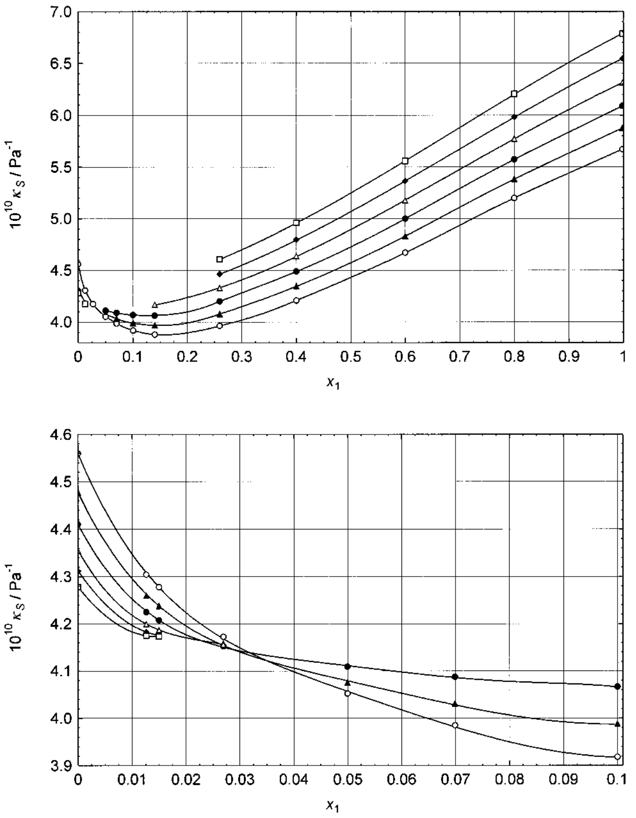

Figure 3. Isotherms of the coefficient of the adiabatic compressibility for 2,6-dimethylpyridine (1) + water (2): symbols as in Figure 1; (top) in the whole concentration range (some points were omitted for clarity), (bottom) in dilute aqueous solutions. The phase separation of 2,6-dimethylpyridine + water at $t > 34$ °C causes some isotherms to be broken.

lated from Kell's polynomial (Kell, 1977). In the calibration procedure, the pycnometer was filled with six different masses of water at constant temperature and the apparatus constants were calculated by the least squares regression from the linear equation:

$$h = V/p - V_0/p \tag{2}$$

where h is the sum of the liquid levels in both the capillaries, V is the volume of water, and p and V_0 are the pycnometer constants, the area of the horizontal cross-section of the capillary and the volume of the pycnometer bulb, respectively. For each temperature of calibration within the limits 293− 318 K a pair of p and V_0 values was determined. During the measurement the pycnometer was held in a water thermostat at constant temperature (±0.01 K). The pycnometer was weighted by an analytical balance, WA-35 (ZMP Gdańsk), with a resolution of 1×10^{-5} g. The air density for the measured ambient temperature and barometric pressure was used in the calculation of the buoyancy correction. The precision of the density measurements was $\pm 5 \times 10^{-3}$ kg m^{-3}, while the accuracy is 10 times lower. It shoud be mentioned that an accuracy of 1×10^{-2} kg m^{-3} in the density measurements is possible only provided the isotopic compositions of both the investigated liquid and the standard one are strictly defined (Kell, 1977).

In the ultrasonic experiment, the temperature was measured by a quartz probe (Zopan, Warsaw) and oscillation frequencies ($f \approx 28$ MHz, $\partial f/\partial T \approx 1$ kHz/K) were determined by the Mera-Tronik C-573 counter−timer. The thermometer was calibrated at the triple point of water; the $(\partial f/\partial T)_P$ slope is given by the manufacturer and checked by measurement of the boiling point of water in the Świętosławski ebulliometer.

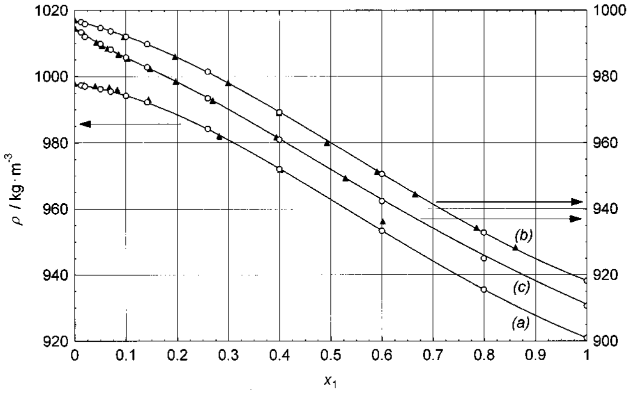

Figure 4. Density of 2,6-dimethylpyridine (1) + water (2): this work, ○; literature, ▲; (a) 22 °C (Grattoni et al., 1993); (b) 25 °C (Abe et al., 1978); (c) 33.5 °C, experimental values and polynomial of Jayalakshmi et al. (1994).

The temperature of the water bath in the densimetric experiment was measured with a resolution of 0.01 K using a Pt(100) thermometer checked against the above described quartz one.

Taking into account the measurement accuracy, the effects caused by the difference between the temperature scales ITS-90 and IPTS-68 are neglible.

Results

The densities (ρ) of and ultrasonic velocities (u) in 2,6-dimethylpyridine (1) + water (2) are listed in Tables 2 and 3, respectively. The dependencies of ρ and u on temperature (T) are satisfactorily approximated by the polynomial

$$y = \sum_{i=0}^{2} a_i (T - 273.15)^i \tag{3}$$

where y is the density/velocity, a_i are the polynomial coefficients calculated by the least squares method and given in Table 4 (where the coefficients $a_i = \rho_i$ for density and $a_i = u_i$ for velocity) together with the extrapolated values for pure 2,6-dimethylpyridine. The t-testing of the regression coefficients indicated that the polynomials of higher degrees are superfluous. In all the following calculations the ρ and c values calculated from polynomial 3 were used. The density and velocity isotherms are plotted in Figures 1 and 2, respectively.

The adiabatic compressibility coefficient, κ_S, was calculated from the Laplace equation:

$$\kappa_S = 1/\varrho u^2 \tag{4}$$

Its isotherms are plotted in Figure 3.

Summary

Good agreement between the measured densities of 2,6-dimethylpyridine (1) + water (2) and those found in the literature is illustrated in Figure 4. The main sources of systematic errors are, in our opinion, impurities of 2,6-dimethylpyridine, in particular other methylpyridines and water.

The density of 2,6-dimethylpyridine (1) + water (2) decreases monotonically with increasing amine concentration (Figure 1). The ultrasonic velocity and compressibility show two points of interest: the nearly common crossing points at $x_1 \approx 0.03$ and the extrema at $x_1 \approx 0.15$, both of them shifting slightly toward lower x_1 values with increasing temperature (Figures 2 and 3). Similar features show the *u* and κ_S isotherms of aqueous solutions of 2- and 4-methylpyridine (Ernst and Marczak, 1992, 1995).

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