J. Chem. Eng. Data 1988, 33, 165-169

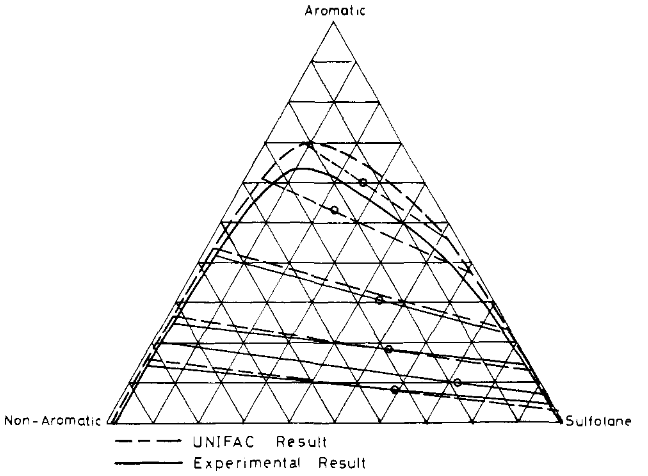

Figure 8. Comparison of predicted and experimental phase compositions of the system aromatics–nonaromatics–sulfolane at 30 °C.

ation until $\sum (X_i^{II}{}_{old} - X_i^{II}{}_{new}) < 10^{-8}$.

Results and Discussion

Figure 8 and Table VII demonstrate that the predicted phase compositions are in good agreement with the corresponding experimental values for the system aromatic–nonaromatic–sulfolane. The deviation of the predicted compositions near the plait point is characteristic of any prediction method but is of little consequence since practical extractions are never carried out near the plait point.

With regard to the effect of temperature on the selectivity and distribution coefficient, the selectivity of sulfolane will decrease with temperature since the heterogeneous area decreases with temperature. The slope of the tie lines is inclined toward the solvent, but the selectivity is greater than one; thus the extraction is possible.

Conclusions

It is concluded from the above results that the temperature had a modest effect on the miscibility range of the systems studied. On balance, considering both capacity and selectivity of sulfolane, with the systems studied better results were achieved at the lowest temperature of 30 °C.

Good agreement was obtained between data predicted by the UNIFAC method and experimental results as shown in Figure 8. The UNIFAC method is presently being applied to predict phase equilibria for actual naphtha cuts. The predicted values will be used to correlate data obtained on the extraction of naphtha by sulfolane, using a mixer-settler cascade. Work is also in progress to improve prediction near the plait point by improving the interaction parameters of UNIFAC.

Glossary

X_{BB}	concentration of solvent B in B phase in eq 1, 2, and 3
X_{AA}	concentration of solvent A in A phase in eq 1, 2, and 3
X_{CA}/X_{AA}	concentration of aromatics in nonaromatics phase per concentration of nonaromatics in nonaromatics phase in eq 4
X_{CB}/X_{BB}	concentration of aromatics in sulfolane phase per concentration of sulfolane in sulfolane phase in eq 4
r, b, n	constants
X_i^F	concentration of component i in feed
I	extract phase
II	raffinate phase
γ	activity coefficient

Registry No. Hexane, 110-54-3; benzene, 71-43-2; heptane, 142-82-5; toluene, 108-88-3; octane, 111-65-9; xylene, 1330-20-7; sulfolane, 126-33-0.

Literature Cited

(1) Voetthr, H.; Kosters, W. C. G. Presented at The Sixth World Petroleum Congress, 1963; Section III, paper II.
(2) Broughton, D.; Asselin, G. F. *7th World Pet. Congr.* **1967**, 65.
(3) Smith, T. E.; Bonner, R. F. *Ind. Eng. Chem.* **1950**, *42*, 896.
(4) Alders, L. *Liquid-liquid Extraction*; Elsevier: London, 1959.
(5) Brancker, A. V.; Hunter, T. G.; Nash, A. W. *Ind. Eng. Chem. Anal. Ed.* **1940**, *35*, 12.
(6) Sherwood, T. K. *Absorption and Extraction*, 1st ed.; McGraw-Hill: New York, 1937.
(7) Hand, P. B. *J. Phys. Chem.* **1930**, *34*, 1961.
(8) Bachman, I. *Ind. Eng. Chem. Anal. Ed.* **1940**, *12*, 38.
(9) Othmer, D. F.; Tobias, P. E. *Ind. Eng. Chem.* **1942**, *34*, 690.
(10) Fredenslund, A.; Jones, R. L.; Prausnitz, J. M. *AIChE* **1975**, *21*, 1086.
(11) Skojold-Jorgensen, S.; Kolbe, B.; Gmehling, J.; Rasmussen, P. *Ind. Eng. Chem. Process Des. Dev.* **1979**, *181*, 714.

Received for review October 27, 1986. Accepted October 18, 1987.

Ultrasonic Velocity and Adiabatic Compressibility of Monochloroacetic Acid in Aqueous Ethanol at Various Temperatures

Pandharinath S. Nikam* and Mehdi Hasan

P. G. Department of Physical Chemistry, M.S.G. College, Malegaon Camp 423 105, District Nasik, India

Ultrasonic velocities of solutions of monochloroacetic acid in aqueous ethanol were measured at 25, 30, 35, and 40 °C by using a single-crystal interferometer at a frequency of 1.5 MHz. The ultrasonic velocity, density, and concentration were used to calculate adiabatic compressibility, intermolecular free length, and apparent molal compressibility. Bachem's relation has been found to be obeyed and the constants *A* and *B* of this relation of various solvents have also been reported.

Introduction

Accurate thermodynamic data on dilute electrolyte solutions are frequently needed. The sound velocity is a purely thermodynamic function. Many other thermodynamic properties of electrolyte solutions are determined from sound velocity (*1*, *2*). In recent years ultrasonic velocity studies in many of the aqueous and nonaqueous electrolytic solutions have led to new insights into the process of ion–ion and ion–solvent interactions (*3*–*11*). Ultrasonic velocity and adiabatic compressibility are quite sensitive to changes in ionic concentrations. Either or

0021-9568/88/1733-0165$01.50/0

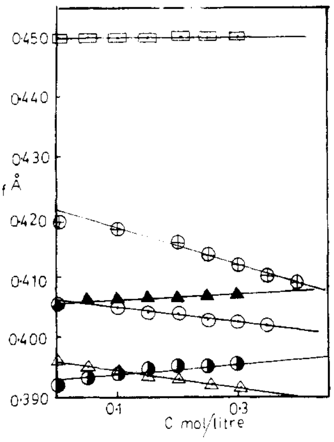

Figure 1. Plot of intermolecular free length versus concentration in water (⊗), 8% ethanol (⊙), 16.4% ethanol (▲), 25.3% ethanol (◑), 34.4% ethanol (▲), and 54.1% ethanol (⊡) at 25 °C.

Table I. Densities, Ultrasonic Velocities, and Related Parameters of $CH_2ClCOOH$ in Water at 25, 30, 35, and 40 °C

C, mol/L	ρ, g/cm³	u, m/s	$\beta_{ad} \times 10^{12}$, cm²/dyn	$\phi_k \times 10^9$, cm²/dyn	L_f, Å
25 °C					
0.0000	0.997 05	1492.2	45.04		0.4194
0.1027	0.999 91	1494.9	44.75	0.187	0.4181
0.2000	1.003 45	1500.3	44.27	−1.026	0.4158
0.2491	1.004 81	1505.4	43.94	−1.354	0.4143
0.2997	1.006 88	1508.7	43.56	−2.151	0.4125
0.3478	1.008 66	1517.4	43.06	−2.932	0.4101
0.4004	1.010 49	1521.1	42.77	−2.917	0.4087
30 °C					
0.0000	0.995 65	1504.5	44.37		0.4203
0.1027	0.998 63	1506.9	44.10	0.289	0.4190
0.2000	1.001 92	1513.8	43.55	−1.286	0.4164
0.2491	1.003 35	1518.9	43.20	−1.863	0.4150
0.2997	1.005 35	1523.4	42.86	−2.269	0.4131
0.3478	1.007 19	1528.8	42.45	−2.702	0.4113
0.4004	1.008 98	1534.2	42.11	−2.917	0.4095
35 °C					
0.0000	0.994 03	1522.5	43.40		0.4190
0.1027	0.997 01	1521.0	43.36	2.469	0.4188
0.2000	1.000 43	1524.6	43.0	0.728	0.4170
0.2491	1.001 75	1520.1	43.20	1.97	0.4180
0.2997	1.003 51	1522.5	42.99	1.383	0.4170
0.3478	1.005 52	1521.3	42.97	1.447	0.4169
0.4004	1.007 31	1526.7	42.59	2.237	0.4151
40 °C					
0.0000	0.992 21	1529.4	43.09		0.4214
0.1027	0.995 25	1533.6	42.72	−0.7848	0.4196
0.2000	0.998 60	1533.6	42.58	0.166	0.4189
0.2491	0.999 60	1532.4	42.59	0.746	0.4190
0.2997	1.001 92	1533.3	42.45	0.562	0.4183
0.3478	1.003 68	1531.8	42.46	0.860	0.4183
0.4004	1.005 40	1532.1	42.37	0.875	0.4179

both of them can be used to detect ionic interaction inclusive of complex formation (*12*, *13*). Recently ionic interaction and ion–solvent interaction in the present system have been reported by Nikam and Mehdi from density and viscosity measurements (*14*). Adiabatic compressibility (β_{ad}), intermolecular free length (L_f), and apparent molal compressibility (ϕ_k) are calculable (*15*) from ultrasonic velocity (u). As these parameters are a more accurate measure of ion–ion and ion–solvent interactions, an ultrasonic study on solutions of monochloroacetic acid in aqueous ethanol of varying dielectric constants has been made at different temperatures.

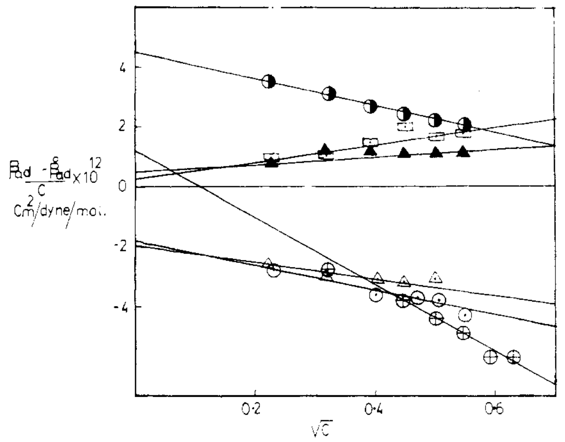

Figure 2. Plot of Bachem's relation in water (⊗), 8% ethanol (⊙), 16.4% ethanol (▲), 25.3% ethanol (◑), 34.4% ethanol (▲), and 54.1% ethanol (⊡) at 25 °C.

Table II. Densities, Ultrasonic Velocities, and Related Parameters of $CH_2ClCOOH$ in 8% Ethanol at 25, 30, 35, and 40 °C

C, mol/L	ρ, g/cm³	u, m/s	$\beta_{ad} \times 10^{12}$, cm²/dyn	$\phi_k \times 10^9$, cm²/dyn	L_f, Å
25 °C					
0.0000	0.983 08	1549.8	42.35		0.4067
0.0534	0.985 05	1551.0	42.20	−0.327	0.4060
0.1026	0.986 89	1552.2	42.06	−0.355	0.4053
0.1608	0.988 57	1556.1	41.78	−0.945	0.4040
0.2230	0.990 72	1558.5	41.56	−0.948	0.4029
0.2574	0.991 86	1560.9	41.38	−1.167	0.4020
0.2888	0.992 79	1565.4	41.10	−1.706	0.4007
30 °C					
0.0000	0.981 62	1552.2	42.28		0.4103
0.0534	0.983 55	1554.3	42.09	−1.044	0.4094
0.1026	0.985 36	1556.7	41.88	−1.398	0.4084
0.1608	0.986 96	1558.2	41.73	−0.780	0.4075
0.2230	0.989 07	1561.5	41.47	−1.001	0.4064
0.2574	0.990 21	1563.0	41.34	−1.019	0.4057
0.2888	0.991 14	1565.1	41.19	−1.124	0.4050
35 °C					
0.0000	0.979 96	1563.0	41.77		0.4110
0.0534	0.981 82	1565.7	41.55	−1.576	0.4100
0.1026	0.983 62	1567.5	41.38	−1.294	0.4091
0.1608	0.985 25	1569.6	41.20	−0.919	0.4082
0.2230	0.987 26	1673.2	40.93	−1.134	0.4069
0.2574	0.988 4	1575.0	40.79	−1.177	0.4062
0.2888	0.989 29	1576.5	40.67	−1.158	0.4056
40 °C					
0.0000	0.978 07	1566.6	41.66		0.4144
0.0534	0.979 89	1568.1	41.56	−0.423	0.4136
0.1026	0.981 55	1569.3	41.37	−0.246	0.4129
0.1608	0.983 11	1570.8	41.22	−0.046	0.4122
0.2230	0.985 22	1572.6	41.04	−0.121	0.4113
0.2574	0.986 28	1575.9	40.83	−0.558	0.4102
0.2888	0.987 18	1578.3	40.66	−0.781	0.4094

Experimental Section

Monochloroacetic acid was recrystallized from hot benzene and dried under vacuum. Melting point determination revealed the α form of the acid. The purified form of the acid was stored in a desiccator under vacuum. The desiccator was fully covered with black paper to prevent even the slightest photolysis of the acid. Water and ethanol purified by standard methods were mixed by weight to give mixtures of different dielectric constants (*16*). Solutions of different molarities were prepared by dissolving accurately known weights of the acid in a solvent

Table III. Densities, Ultrasonic Velocities, and Related Parameters of $CH_2ClCOOH$ in 16.4% Ethanol at 25, 30, 35, and 40 °C

C, mol/L	ρ, g/cm^3	u, m/s	$\beta_{ad} \times 10^{12}$, cm^2/dyn	$\phi_k \times 10^9$, cm^2/dyn	L_f, Å
25 °C					
0.0000	0.970 78	1597.2	40.38		0.3972
0.0504	0.972 32	1597.8	40.28	−0.676	0.3965
0.0984	0.974 22	1600.2	40.09	−0.470	0.3957
0.1627	0.977 29	1601.7	39.88	−0.808	0.3947
0.1999	0.978 28	1603.8	39.74	−0.834	0.3940
0.2501	0.979 73	1605.3	39.61	−0.637	0.3934
0.2999	0.981 65	1607.4	39.43	−0.745	0.3925
30 °C					
0.0000	0.968 74	1600.5	40.30		0.4006
0.0504	0.970 17	1602.0	40.16	−0.027	0.3999
0.0984	0.972 16	1603.5	40.00	−0.563	0.3991
0.1627	0.975 2	1605.3	39.79	−0.855	0.3980
0.1999	0.976 12	1608.0	39.62	−1.006	0.3972
0.2501	0.977 57	1609.5	39.49	−0.816	0.3965
0.2999	0.979 82	1611.9	39.28	−0.007	0.3955
35 °C					
0.0000	0.966 6	1602.3	40.30		0.4037
0.0504	0.968 03	1602.6	40.22	1.170	0.4033
0.0984	0.969 92	1603.5	40.10	0.501	0.4027
0.1627	0.972 91	1605.3	39.88	−0.258	0.4016
0.1999	0.973 79	1605.9	39.82	−0.039	0.4013
0.2501	0.975 31	1609.8	39.56	0.471	0.4000
0.2999	0.977 19	1612.8	39.34	−0.733	0.3984
40 °C					
0.0000	0.964 24	1603.8	40.32		0.4076
0.0504	0.965 6	1604.4	40.23	1.038	0.4072
0.0984	0.967 51	1605.3	40.11	0.428	0.4066
0.1627	0.970 40	1606.5	39.93	−0.029	0.4057
0.1999	0.971 28	1608.0	39.82	−0.022	0.4051
0.2501	0.972 66	1610.1	39.66	−0.095	0.4043
0.2999	0.974 44	1614.0	39.40	−0.538	0.4030

Table IV. Densities, Ultrasonic Velocities, and Related Parameters of $CH_2ClCOOH$ in 25.3% Ethanol at 25, 30, 35, and 40 °C

C, mol/L	ρ, g/cm^3	u, m/s	$\beta_{ad} \times 10^{12}$, cm^2/dyn	$\phi_k \times 10^9$, cm^2/dyn	L_f, Å
25 °C					
0.0000	0.958 69	1626.6	39.42		0.3924
0.0516	0.960 51	1621.5	39.60	5.924	0.3933
0.1031	0.962 02	1617.3	39.74	5.661	0.3940
0.1505	0.963 25	1614.6	39.82	5.296	0.3944
0.2002	0.964 97	1611.6	39.90	4.993	0.3948
0.2503	0.967 02	1608.3	39.98	4.755	0.3952
0.2999	0.968 32	1605.6	40.06	4.699	0.3956
30 °C					
0.0000	0.956 01	1619.1	39.90		0.3986
0.0516	0.957 69	1614.0	40.03	0.074	0.3995
0.1031	0.959 20	1610.1	40.22	5.756	0.4002
0.1505	0.960 42	1606.5	40.34	5.645	0.4008
0.2002	0.962 14	1603.2	40.44	5.363	0.4013
0.2503	0.964 11	1599.9	40.52	5.070	0.4017
0.2999	0.965 41	1597.2	40.60	4.970	0.4021
35 °C					
0.000	0.953 14	1608.3	40.56		0.4050
0.0516	0.954 86	1602.6	40.78	6.866	0.4061
0.1031	0.956 3	1597.8	40.96	6.597	0.4070
0.1505	0.957 47	1594.2	41.10	6.385	0.4072
0.2002	0.959 03	1591.2	41.18	5.866	0.4081
0.2503	0.961 19	1587.6	41.28	5.499	0.4086
0.2999	0.962 39	1585.5	41.34	5.312	0.4089
40 °C					
0.0000	0.950 13	1599.6	41.13		0.4117
0.0516	0.951 75	1595.7	41.26	5.251	0.4124
0.1031	0.953 18	1593.0	41.34	4.845	0.4128
0.1505	0.954 41	1590.6	41.41	4.720	0.4131
0.2002	3.950 07	1588.2	41.47	4.505	0.4134
0.2503	0.958 06	1585.8	41.51	4.238	0.4136
0.2999	0.958 99	1584.3	41.54	4.179	0.4138

Table V. Densities, Ultrasonic Velocities, and Related Parameters of $CH_2ClCOOH$ in 34.4% Ethanol at 25, 30, 35, and 40 °C

C, mol/L	ρ, g/cm^3	u, m/s	$\beta_{ad} \times 10^{12}$, cm^2/dyn	$\phi_k \times 10^9$, cm^2/dyn	L_f, Å
25 °C					
0.0000	0.942 66	1587.3	42.10		0.4055
0.0503	0.944 44	1565.2	42.14	3.435	0.4057
0.0998	0.946 04	1582.2	42.22	3.910	0.4061
0.1503	0.947 7	1579.8	42.28	3.920	0.4064
0.2012	0.949 07	1576.3	42.30	3.792	0.4065
0.2502	0.953 02	1576.0	42.36	3.892	0.4068
0.2995	0.952 0	1573.6	42.42	3.896	0.4071
30 °C					
0.0000	0.939 28	1586.7	42.29		0.4103
0.0503	0.941 06	1583.2	42.40	5.445	0.4110
0.0998	0.942 64	1580.4	42.47	4.542	0.4112
0.1503	0.944 30	1577.7	42.54	4.414	0.4116
0.2012	0.945 63	1573.8	42.70	4.872	0.4123
0.2502	0.946 94	1572.3	42.72	4.595	0.4124
0.2995	0.948 58	1569.6	42.79	5.419	0.4128
35 °C					
0.0000	0.935 92	1582.2	42.68		0.4155
0.0503	0.937 69	1580.4	42.70	3.102	0.4156
0.0998	0.939 27	1578.0	42.76	3.580	0.4159
0.1503	0.940 83	1575.3	42.83	3.818	0.4162
0.2012	0.942 25	1572.6	42.91	4.075	0.4168
0.2502	0.943 49	1570.2	42.99	4.169	0.4170
0.2995	0.945 16	1567.7	43.05	4.138	0.4173
40 °C					
0.0000	0.932 33	1580.4	42.94		0.4270
0.0503	0.934 1	1574.9	43.02	4.322	0.4211
0.0998	0.935 63	1573.5	43.16	5.134	0.4218
0.1503	0.937 22	1571.4	43.21	4.650	0.4220
0.2012	0.938 57	1569.0	43.28	4.614	0.4224
0.2502	0.939 77	1566.6	43.36	4.662	0.4228
0.2995	0.941 54	1563.3	43.46	4.672	0.4232

Table VI. Densities, Ultrasonic Velocities, and Related Parameters of $CH_2ClCOOH$ in 54.1% Ethanol at 25, 30, 35, and 40 °C

C, mol/L	ρ, g/cm^3	u, m/s	$\beta_{ad} \times 10^{12}$, cm^2/dyn	$\phi_k \times 10^9$, cm^2/dyn	L_f, Å
25 °C					
0.0000	0.900 29	1461.1	52.03		0.4609
0.0502	0.902 60	1458.6	52.08	3.599	0.4510
0.0998	0.904 64	1455.9	52.15	4.045	0.4513
0.1543	0.905 94	1453.2	52.27	4.836	0.4519
0.2019	0.907 24	1449.6	52.45	5.503	0.4526
0.2496	0.909 40	1447.8	52.46	5.036	0.4527
0.2997	0.910 88	1444.8	52.59	5.255	0.4532
30 °C					
0.0000	0.896 3	1450.2	53.05		0.4596
0.0502	0.899 66	1446.6	53.18	5.400	0.4602
0.0998	0.900 68	1444.2	53.23	4.799	0.4604
0.1543	0.902 12	1441.2	53.37	5.435	0.4610
0.2019	0.903 42	1437.6	53.56	6.032	0.4618
0.2496	0.905 55	1435.8	53.57	5.483	0.4618
0.2997	0.906 89	1433.7	53.65	5.470	0.4622
35 °C					
0.0000	0.892 29	1438.2	54.18		0.4681
0.0502	0.894 68	1435.8	54.22	3.644	0.4683
0.0998	0.896 62	1433.4	54.28	4.186	0.4686
0.1543	0.898 09	1431.0	54.38	4.752	0.4690
0.2019	0.899 36	1429.2	54.43	4.900	0.4692
0.2496	0.901 50	1425.3	54.60	5.180	0.4700
0.2997	0.902 87	1423.2	54.68	5.263	0.4703
40 °C					
0.0000	0.888 24	1434.9	54.68		0.4747
0.0502	0.890 59	1432.8	54.70	3.334	0.4748
0.0998	0.892 54	1430.4	54.76	3.967	0.4751
0.1543	0.893 95	1427.7	54.88	4.836	0.4756
0.2019	0.895 18	1425.6	54.97	5.128	0.4760
0.2496	0.897 44	1422.0	55.11	5.271	0.4766
0.2997	0.898 76	1419.0	55.26	5.592	0.4772

Table VII. A, B, ϕ_k^0, and S_k Values[a]

	25 °C				30 °C				35 °C				40 °C			
system	A	B	$\phi_k^0 \times 10^9$	$S_k \times 10^9$	A	B	$\phi_k^0 \times 10^9$	$S_k \times 10^9$	A	B	$\phi_k^0 \times 10^9$	$S_k \times 10^9$	A	B	$\phi_k^0 \times 10^9$	$S_k \times 10^9$
water	0.4	-9.66	4.9	-10.67	0.8	-10.62	1.8	-7.59	1.05	-4.67	-0.1	-4.89	0.2	-5.0	-2.7	6.182
8% ethanol	-2.2	-3.03	0.5	-3.42	-2.2	-3.03	0.2	-2.36	-2.35	-3.03	0.05	-2.30	-1.0	-4.29	1.05	-3.43
16.4% ethanol	-2.1	-2.35	-0.05	-1.29	-2.3	-2.22	0.0	-1.87	-0.7	-4.38	2.6	-6.15	-0.9	-3.70	1.45	-3.46
25.3% ethanol	4.5	4.57	6.75	-3.85	4.3	3.87	6.85	-3.33	5.5	5.18	8.1	-5.0	3.4	4.0	5.75	-2.9
34.4% ethanol	0.05	0.35	1.47	3.25	0.19	1.29	1.8	6.67	-0.21	0.77	2.36	3.65	1.49	0.436	4.0	1.62
54.1% ethanol	0.3	2.67	2.6	45.45	0.8	3.56	4.9	12.12	1.76	2.67	2.3	55.56	0.72	4.69	1.9	69.56

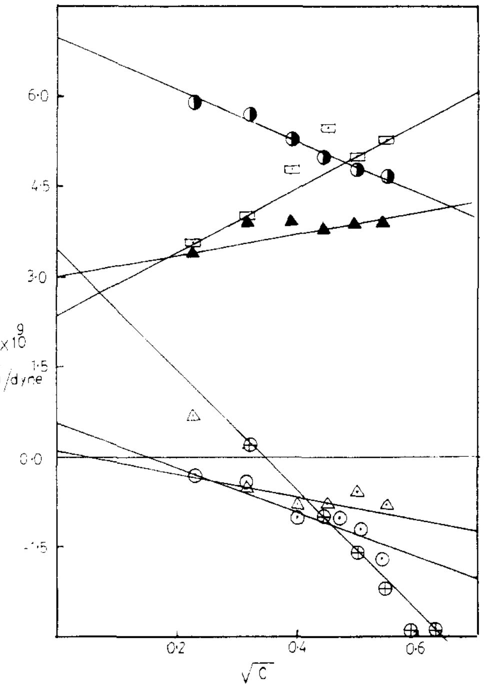

Figure 3. Plot of apparent molal compressibility versus square root of concentration in water (⊗), 8% ethanol (⊙), 16.4% ethanol (△), 25.3% ethanol (◑), 34.4% ethanol (▲), and 54.1% ethanol (⊡) at 25 °C.

mixture and kept for some time. The densities were measured pycnometrically with an accuracy of 1 in 10^{-4}.

The velocities of ultrasonic waves of frequency 1.5 MHz in these solutions were measured by the interferometer method using Mittal's M-82 instrument at different temperatures in the range 25–40 °C. The error in these measurements is ±0.03%.

Results and Discussion

The variation of ultrasonic velocity in a solution depends upon the increase or decrease of intermolecular free lengths after mixing the components. On the basis of a model for sound propagation proposed by Eyring and Kincaid (*17*), ultrasonic velocity should increase if the intermolecular free length decreases as a result of mixing of components. They have indicated that intermolecular free length is a predominant factor in determining the variation of ultrasonic velocity in a solution. In the present investigation it has been observed that intermolecular free length decreases on increasing the concentration of monochloroacetic acid solutions in 0, 8, and 16.4 wt % solvent mixtures (Tables I–III). Figure 1 shows the intermolecular free length–concentration relationship for the monochloroacetic acid solutions prepared in 0, 8, and 16.4 wt % solvent mixtures at 25 °C. This trend is observed at all temperatures. This behavior indicates significant interaction between solute and solvent molecules, suggesting a structure-promoting tendency of the added electrolyte. However, intermolecular free length increases on increasing the concentration of monochloroacetic acid which results in a decrease of ultrasonic velocity in solutions in 25.3, 34.4, and 54.1 wt % solvent mixtures. Tables IV–VI present this relationship which is also represented by Figure 1. This implies a decrease in the number of free ions and hence the occurrence of ionic association due to strong ion–ion interactions. Here the added electrolyte exhibits a structure breaking tendency.

Solutions in the 0, 8, and 16.4 wt % solvent mixtures show increase in ultrasonic velocity with increase in temperature for the same concentration, suggesting ion–solvent interaction, while those in the 25.3, 34.4, and 54.1 wt % solvent mixtures show decrease in ultrasonic velocity with increases in temperature favoring strong ion–ion interaction.

As expected β_{ad} decreases with increase of concentration in solutions in 0, 8, and 16.4 wt % solvent mixtures (Tables I–III) supporting solute–solvent interactions. On the other hand adiabatic compressibility increases with increase of concentration in solutions of 25.3, 34.4, and 54.1 wt % solvent mixtures (Tables IV–VI). This indicates the strong ion–ion interactions in these solutions.

The adiabatic compressibility of solutions studied here are found to obey Bachem's relation (*18*): $\beta_{ad} = \beta_{ad}^0 + AC + BC^{3/2}$ where C is the molar concentration, A and B are constants, and β_{ad} and β_{ad}^0 are adiabatic compressibilities of solution and solvent, respectively. When $\beta_{ad} - \beta_{ad}^0/C$ is plotted against $C^{1/2}$, a linear variation has been noted in each case. The slopes and intercepts of the curves have positive as well as negative signs (Table VII). Figure 2 gives the verification of Bachem's relation for all systems.

Figure 3 represents the variation of apparent molal compressibility with the square root of concentration which is more or less linear for all systems studied at all temperatures. Thus monochloroacetic acid solutions in 0.8, 16.4, 25.3, 34.4, and 54.1 wt % solvent mixtures obey Gucker's limiting law (*19*), namely $\phi_k = \phi_k^0 + S_kC^{1/2}$. The limiting apparent molal compressibilities (ϕ_k^0) are positive in sign having varying magnitudes in solutions in 0,8, 16.4, and 25.3 wt % solvent mixtures indicating a predominance of solute solvent interaction. Slopes of these graphs (S_k) are negative in sign suggesting negligible ionic association. Slope (S_k) and intercept (ϕ_k^0) values are positive in solutions in 34.4 and 54.1 wt % solvent mixtures confirming the strong ion–ion interaction dominating solute–solvent interaction. This may be attributed to the lower dielectric constants of the medium (increase in ethanol content). Since low dielectric constant promotes electrostatic attraction, it is quite reasonable to obtain positive slopes. Table VII gives ϕ_k^0 and S_k values for all systems at all temperatures.

Acknowledgment

We gratefully acknowledge Principal R. V. Khairnar for his constant encouragement and facilities provided.

Registry No. Monochloroacetic acid, 79-11-8; ethanol, 64-17-5.

J. Chem. Eng. Data 1988, 33, 169–173

Literature Cited

(1) Nazdrev, V. F. *Application of Ultrasonics in Molecular Physics*; Gordan and Breach: New York, 1963.
(2) Synder, S. J.; Synder, J. R. *J. Chem. Eng. Data* **1974**, *19*, 270.
(3) Gnananba, S.; Rao, B. R. *Indian J. Pure Appl. Phys.* **1969**, *7*, 468.
(4) Agarwal, S. B.; Bhatnagar, V. P. *Jpn. J. Appl. Phys.* **1978**, *15*, 237.
(5) Satyavati, A. V. *Acustica* **1977**, *38*, 340.
(6) Kraus, P.; M. McGuire, M. J. *Can. J. Chem.* **1978**, *56*, 1881.
(7) Fogg, P. G. T. *J. Chem. Soc.* **1958**, 411.
(8) Mikhailov, I. G.; Rozina, M. V.; Shutilow, V. A. *Akust. Zh.* **1964**, *10*, 213.
(9) Allan, D. S.; Lee, W. *J. Chem. Soc.* **1964**, *2*, 6049.
(10) Prakash, S.; Prakash, O. *Acustica* **1975**, *32*, 279.
(11) Srivastava, T. N.; Singh, R. P.; Swaroop, B. *Indian J. Pure Appl. Phys.* **1983**, *21*, 67.
(12) Kaulgud, M. V.; Patil, K. J. *Acustica* **1973**, *28*, 130.
(13) Andreo, J. H.; Edmonds, P. D.; Mickeller, J. T. *Acustica* **1965**, *15*, 74.
(14) Nikam, P. S.; Mehdi Hasan *Curr. Sci.* **1984**, *53*, 260.
(15) Marks, G. W. J. *J. Acoust. Soc. Am.* **1959**, *31*, 936.
(16) Mandal, A. K.; Lahiri, S. C. *Indian J. Chem.* **1977**, *15*, 728.
(17) Eyring, H.; Kincaid, J. F. *J. Chem. Phys.* **1938**, *6*, 620.
(18) Bachem. *Z. Elektrochem.* **1935**, *41*, 570.
(19) Gucker (Jr.), F. T. *Chem. Rev.* **1933**, *13*, 111.

Received for review October 10, 1985. Accepted October 7, 1987.

Ultrasonic Speeds in Liquid Monochlorodifluoromethane (R22) and Monochloropentafluoroethane (R115) under High Pressures

Toshiharu Takagi* and Hiroshi Teranishi

Department of Chemistry, Faculty of Engineering and Design, Kyoto Institute of Technology, Matsugasaki, Sakyoku, Kyoto 606, Japan

The ultrasonic speeds in liquid monochlorodifluoromethane (R22) and monochloropentafluoroethane (R115) were measured by using a sing-around technique employing a fixed-path ultrasonic interferometer of 2 MHz. The results cover every 5 K in the range of temperatures from 283.15 to 323.15 K and pressures from near their saturated vapor pressures to about 50 MPa. The experimental uncertainty of ultrasonic speed was estimated to be no greater than ±0.34% up to 10 MPa and ±0.23% above 10 MPa. From the experimental results, the isentropic compressibility and the ratio of heat capacities were determined by using the *pVT* data reported elsewhere. The present results were compared with our previous results for R502, an azeotropic refrigerant mixture of R22 and R115.

Introduction

In an earlier paper, we reported the temperature and pressure effects of the ultrasonic speed and the isentropic compressibility for compressed liquid R502 (*1*). This refrigerant is the azeotropic mixture of 48.8 wt % (63 mol %) monochlorodifluoromethane, R22, and 51.2 wt % (37 mol %) monochloropentafluoroethane, R115. For these refrigerants, the studies on experimental *pVT* and/or the formulation of an equation of state have been investigated in wide ranges of temperature and pressure (*2*, *3*). However, the direct measurement on thermodynamic properties in connection with the variation due to pressure has scarcely been reported. In this paper, the ultrasonic speeds in the liquid phase for R22 and R115 were measured in the range of temperatures from 283.15 to 323.15 K and pressures from near the saturated vapor pressure to about 50 MPa. From the experimental speed, the isentropic compressibility and the ratio of heat capacities were determined by using the *pVT* data reported elsewhere. The temperature, pressure, and composition dependences of these quantities were examined in comparison with those of R502 observed in our recent work (*1*).

Table I. Physical Properties of Each Compound

	R22	R115	R502[a]
chemical formula	$CHClF_2$	$CClF_2{-}CF_3$	R22/R115
molecular weight	86.48	154.48	111.64
dipole moment,[b] 10^{-30} C·m	4.73	1.73	
critical constants[c]			
temp, K	369.15	353.15	355.35
press., MPa	4.98	3.23	4.08
density, $kg{\cdot}m^{-3}$	524	613	561

[a] Azeotropic mixture refrigerant. [b] Reference *4*. [c] Reference *3*.

Experimental Section

Material. Monochlorodifluoromethane, $CHClF_2$ (R22), and monochloropentafluoroethane, $CClF_2{-}CF_3$ (R115), were supplied by Daikin Kogyo Co. Their purities were better than 99.9 wt % as measured by GLC. The physical properties of each refrigerant are listed in Table I together with those of R502.

Apparatus. The method used for measurement of ultrasonic speed was a sing-around technique with fixed-path ultrasonic interferometer employing a single transducer, similar to that described previously (*5*). The measurements were covered in detail over the range of temperature from 283.15 to 323.15 K and pressures from near the saturated vapor pressure to about 50 MPa. The uncertainty in temperature measurements of the sample was less than ±0.03 K. The uncertainties of pressure, measured by a precise bourdon gauge and a strain gauge, were estimated to be no greater than ±0.03 MPa in the range up to 5 MPa and ±0.12 MPa above 5 MPa to 50 MPa. The probable uncertainty due to the instrument used in this work was confirmed by measuring the speed in pure benzene to be less than ±1.3% under all present experimental conditions (*5*).

Results and Discussion

The experimental values of the ultrasonic speeds *u* in the liquid phase of monochlorodifluoromethane (R22) and monochloropentafluoroethane (R115) at several temperatures *T* and

0021-9568/88/1733-0169$01.50/0