erally decrease with the increase in temperature except for the ternary *n*-hexane (1)–toluene (2)–1-hexanol (3), for which the trend is reversed. Further, a comparison of the deviations for the ternaries studied (Table VI) with those of their binary subsystems reported earlier (*1*) shows that in the case of *n*-hexane (1)–chlorobenzene (2)–1-hexanol (3) and toluene (1)–chlorobenzene (2)–1-hexanol (3), systems, the order of the magnitudes of rms deviations is the same as that for their binary subsystems while for the *n*-hexane (1)–toluene (2)–chlorobenzene (3) system the rms deviations are somewhat higher than those obtained for the corresponding binary subsystems. Thus, eq 1 can safely be employed to predict the dependence of ternary dielectric constants on the composition and temperature for the systems studied when no ternary or binary experimental dielectric constant data are readily available.

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Glossary

k	Boltzmann constant
n	refractive index
G	SLS correlation parameter (eq 1)
M	molecular weight
N	Avogadro's number
T	absolute temperature
V	molar volume at the temperature of investigation, $cm^3\ mol^{-1}$
V_s	molar volume of a substance just before melting, $cm^3\ mol^{-1}$
X_i	mole fraction of component i
rmsd	room mean square deviation
K	number of data

Greek Letters

ϵ	dielectric constant
μ	dipole moment of the free molecule, D

Subscripts

D	for sodium light
i, j	component in a mixture
m	mixture
1, 2, 3	component numbers in a mixture

Registry No. *n*-Hexane, 110-54-3; toluene, 108-88-3; chlorobenzene, 108-90-7; 1-hexanol, 111-27-3.

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Densities of Aqueous Solutions of NaCl, $MgCl_2$, KCl, NaBr, LiCl, and $CaCl_2$ from 0.05 to 5.0 mol kg^{-1} and 0.1013 to 40 MPa at 298.15 K

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The density differences, $\Delta\rho = \rho - \rho_0$ (where ρ = density of the solution and ρ_0 is the density of H_2O), of NaCl, $MgCl_2$, KCl, NaBr, LiCl, and $CaCl_2$ aqueous solutions have been measured from 0.1013 to 40 MPa and for molalities of 0.05–5.0 mol kg^{-1} at 298.15 K. ($MgCl_2$ and KCl molality ranges were 0.05–3.0 mol kg^{-1}.) These results have been least-squares fitted by a polynomial equation in molality and pressure, with standard errors less than 50 × 10^{-6} g cm^{-3}. A comparison of these equations with available literature data is also included.

Introduction

Densities of aqueous electrolyte solutions at room temperature and atmospheric pressure are readily available (*1–8*). Reliable measurements have been made for a variety of systems at elevated pressure (*7–10*). Unfortunately, these measurements have been confined to narrow concentration ranges at low concentration (with the exception of NaCl). Sound velocity measurements have been made on all of these salts at 25 °C and atmospheric pressure (*11*, *12*) (NaCl and $MgCl_2$ sound velocities have been measured as a function of pressure to 1.0 mol kg^{-1}) (*13*). The purpose of this research is to obtain density measurements at room temperature and elevated pressures (0.1–40 MPa) over a wide concentration range (0.05–5.0 mol kg^{-1}). These data are required for calculations involved with mass flow calorimeters and high-temperature mercury displacement type densimeters (*14–16*). The results presented in this paper were measured on a vibrating tube type densimeter. Empirical fits of these measurements are also included.

Experimental Section

The vibrating tube densimeter, designed and built by H. J. Albert, has been described in detail elsewhere (*18*). The addition of a NESLAB Endocal refrigerated circulating bath to cool the outer jacket of the densimeter was the only modification required to run this instrument at 298 K. The instrument was calibrated, as is necessary for all vibrating tube type densimeters, by using water (*19*) and nitrogen at experimental pressure

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(*18*). The uncertainty in the density of the nitrogen at high pressure results in an estimated uncertainty of 0.1% in the calibration constant and thus 0.1% in the difference in density between the solution and water, $\Delta\rho = \rho - \rho_0$, which is directly measured.

In all cases degassed, distilled, deionized water was used to establish a reference base line. An HPLC injection valve (Rheodyne 7010) was employed to introduce a 6-mL sample of solution into the inlet stream after which a water base line was reestablished. Experiments with differences in the two water base lines larger than 1 part in 100 000 were not acceptable. The solutions, originally run on our heat capacity calorimeter, were made from reagent-grade salts without further purification. The concentrations were determined volumetrically to an accuracy of 0.1% (this produces an error of 0.1% in $\Delta\rho$). (The 2.952 mol kg^{-1} $MgCl_2$ solutions are believed to have an accuracy of 0.2%.) The pressure was maintained with a Circle Seal Controls back-pressure regulator and measured with an in-line McDaniel test gauge with an accuracy of approximately 0.3 MPa. (This pressure error results in a maximum error of 30 ppm in $\Delta\rho$. At high concentrations the error is always less than 0.03% in $\Delta\rho$.) The temperature was maintained constant to better than 0.001 K, as measured with a Burns RTD and verified against a Rosemount platinum resistance temperature standard (Model 162CE).

Results

The values of $\Delta\rho$ determined in our laboratory are presented in Table I. These results are the average of several runs which normally agreed to better than 20 ppm (95% confidence limits $\approx$40 ppm). The corresponding calculated values from the empirical fit of the data are also presented in Table I.

For each salt the $\Delta\rho$ data were fitted to an empirical equation of the form

$$\Delta\rho = am/m^\theta + b(m/m^\theta)^{3/2} + c(m/m^\theta)^2 + d(m/m^\theta)P + e(m/m^\theta)^{3/2}P + f(m/m^\theta)P^2 \quad (1)$$

where m is the molality (mol kg^{-1}), $m^\theta = 1.0$ mol kg^{-1}, and P is the pressure in MPa. The standard error of each fit was on the order of 50 ppm and at least 95% of the residuals were less than 40 ppm or 0.1% of $\Delta\rho$ as expected. (The exception to this was the $MgCl_2$ fit with standard error of 65 ppm.) The coefficients for each fit are presented in Table II along with the estimated error of each coefficient and the standard error of the fit. In all cases weighting each point equivalently seemed to yield an acceptable fit. However, various weighting schemes were attempted, none of which improved the overall fit.

Discussion

Reconciliation of volumetric data from two sources is often difficult. Not only do experimental conditions vary, but both the presentation and the representation of the data with a fitting scheme vary from author to author, making comparisons difficult.

The following are comparisons of our representations of our data with other available literature data (or literature data fits), allowing us to evaluate our calculated $\Delta\rho$ at precisely the conditions under which the literature measurements were made. (Solution densities and apparent molar volumes were also calculated, by using the equation of state of water given by Haar, Gallagher, and Kell (*19*), thus allowing comparison with literature data not presented as $\Delta\rho$.)

The literature data base for aqueous NaCl is by far the most extensive, thus allowing for the most thorough comparison (Figure 1A–E). Our calculated $\Delta\rho$'s at 0.1 MPa are slightly higher than the values reported by Perron, Roux, and Desnoyers (*1*); however, agreement is everywhere better than 0.2% in $\Delta\rho$. Our fit also represents the data of LoSurdo, Alzola, and Millero (*2*) to within the errors of the fit and the recent data of Romankiw and Chou (*3*) within their experimental errors (Figure 1A). Gibson and Loeffler's (*7*) volumes of NaCl as functions of pressure allow for another check of our high-pressure results. Our fit is in reasonable agreement with Gibson and Loeffler's data at all pressures (Figure 1A,C,E). Our fit was compared with the tabulated volumes of Rogers and Pitzer (*9*) (Figure 1A,C,E). At 0.1 MPa the agreement between the two fits is good, and at high pressures the two fits agree within their estimated errors. Chen and Millero's equation of state of aqueous NaCl solutions (up to 1.0 mol kg^{-1}) (*13*) demonstrates excellent agreement at all pressures. The earlier data of Chen, Emmet, and Millero (*10*) show systematic deviations from the other investigations. It appears that their data for concentrations of 0.1299 and 0.2507 mol kg^{-1} are in error.

A comparison of our $MgCl_2$ density fit with the data of Chen et al. (*10*) indicates reasonable agreement (within the 70 ppm errors of our fit) over the entire range of comparison (Figure 1G,H). (It should be noted that Chen et al.'s highest molality was 0.315 mol kg^{-1}.) At atmospheric pressure the data of Perron et al. (*1*) and those of LoSurdo et al. (*2*) have been used for comparison (Figure 1F). In both cases our fit represented the data well below 0.6 and above 2.0 mol kg^{-1}. Between 1.0 and 2.0 mol kg^{-1} our fit and our data points are consistently lower than both of these sets of data. Our fit agrees with the data of Romankiw and Chou (*3*) within their experimental errors. Comparison with the equation of state of Chen and Millero (*13*) indicates their results are consistently higher than ours (at 20 MPa and 1.0 mol kg^{-1} their result is 0.7% higher in $\Delta\rho$). On the other hand, the $\Delta\rho$ calculated from Millero, Ricco, and Schreiber's (*12*) compressibilities compare favorably with our fit (all errors less than 0.2% in $\Delta\rho$).

Chen et al. (*10*) also published KCl volumetric data (up to 1.0 mol kg^{-1}) and a fit of that data. Comparison with our KCl fit indicated that our fit either better represented their data or deviated by less than 80 ppm from their fit (Figure 1J,K). A comparison with Vaslow's (*5*) atmospheric apparent molar volume data indicates good agreement with all errors less than 0.08 mL mol^{-1}. (In general, agreement was 0.1% above 1.0 mol kg^{-1} and 0.2% below 1.0 mol kg^{-1}.) Fortier, Leduc, and Desnoyers (*4*) also measured KCl $\Delta\rho$'s, which agree well with our fit (the largest residual being 57 ppm) although our calculated values were consistently low. As with NaCl and $MgCl_2$, a comparison with Romankiw and Chou (*3*) indicated agreement within their specified errors (Figure 1I).

Our NaBr density fit was compared to the high-pressure volume data published by Gibson and Loeffler (*7*) (Figure 1L,M). Gibson and Leffler's interpolated values at 25 MPa were consistently high in $\Delta\rho$ by 0.4%. Extrapolation of our fit to 50 MPa provided good agreement with Gibson and Loeffler's actual measurements. A more extensive comparison at atmospheric pressure was undertaken by using the densities of Robison and Weston (*6*) (Figure 1L). Our fit agreed to within 0.1% in $\Delta\rho$ or 30 ppm, although we tended to be slightly positive at the low concentrations. Fortier et al.'s (*4*) published $\Delta\rho$'s provide the final comparison which resulted in excellent agreement (the largest deviation being 37 ppm).

Our LiCl fit was compared to data of both Vaslow (*5*) and Fortier et al. (*4*). In both cases the agreement was beter than one could hope for, with deviations less than 0.1% in $\Delta\rho$ or 10 ppm for Vaslow's data and all deviations less than 27 ppm for Fortier et al.'s data (Figure 1N).

The $CaCl_2$ fit was initially compared with the data of Perron et al. (*1*) and found to agree within the errors of our fit. Our fit tends to be too positive at high concentrations (about 250 ppm high above 3.5 mol kg^{-1}) (Figure 1P). Romankiw and Chou's (*3*) recent $CaCl_2$ data tend to be quite high, deviating

Table I. Experimental Data

m/(mol kg^{-1})	P, MPa	n^a	$10^3(\Delta\rho)$/(g cm^{-3})	Δb/ppm	ϕ_v^c/(cm^3 mol^{-1})
			(A) NaCl		
4.991	0.1013	2	169.022	−3	20.99
3.023	0.1013	2	109.606	59	19.96
1.994	0.1013	2	75.038	0	19.31
1.021	0.1013	2	40.078	102	18.39
0.4708	0.1013	2	18.936	−9	17.82
0.2880	0.1013	2	11.728	7	17.45
0.0997	0.1013	2	4.102	−18	17.16
0.0582	0.1013	2	2.407	−9	16.97
4.991	10.38	2	167.659	−100	21.29
3.023	10.38	2	108.595	−77	20.34
1.994	10.38	2	74.418	3	19.69
1.021	10.38	3	39.592	−35	18.95
0.4708	10.38	2	18.730	−43	18.35
0.2880	10.38	3	11.603	−10	17.98
0.0997	10.38	2	4.063	−18	17.66
0.0582	10.38	2	2.382	−11	17.51
4.991	17.13	3	167.132	117	21.43
3.023	17.13	2	108.145	−6	20.52
1.994	17.13	2	74.073	33	19.91
1.021	17.13	2	39.407	−9	19.18
0.4708	17.13	2	18.631	−38	19.92
0.2880	17.13	2	11.517	−30	18.34
0.0997	17.13	2	4.034	−23	18.01
0.0582	17.13	2	2.360	−19	17.95
4.991	30.69	3	165.686	−51	21.75
3.023	31.03	2	107.221	7	20.89
1.994	31.04	2	73.374	17	20.33
1.021	31.09	2	39.034	8	19.64
0.4708	31.11	2	18.471	−3	19.07
0.2880	31.09	2	11.436	13	18.74
0.0997	31.13	2	4.004	−8	18.43
0.0582	31.13	2	2.369	17	17.93
4.991	40.78	3	164.983	13	21.92
3.023	40.02	2	106.687	−18	21.10
1.994	40.13	2	72.980	2	20.57
1.021	40.28	2	38.835	32	19.89
0.4708	40.47	2	18.369	10	19.35
0.2880	40.59	2	11.346	−3	19.12
0.0997	40.68	2	3.988	3	18.67
0.0582	39.92	2	2.350	13	18.33
			(B) $MgCl_2$		
2.952	0.1013	3	195.012	18	24.29
2.262	0.1013	2	154.391	60	23.23
0.9917	0.1013	2	72.643	95	20.33
0.4893	0.1013	2	37.121	4	18.49
0.2518	0.1013	2	19.483	−52	17.32
0.0912	0.1013	2	7.169	−60	16.29
0.0312	0.1013	2	2.476	−31	15.68
2.952	10.44	2	193.363	−101	24.95
2.262	10.38	2	152.878	−176	24.01
0.9917	10.38	3	71.880	8	21.28
0.4893	10.38	2	36.733	−17	19.52
0.2518	10.38	2	19.270	−65	18.42
0.0912	10.38	2	7.102	−50	17.31
0.0312	10.38	3	2.461	−19	16.44
2.952	17.27	2	192.681	116	25.26
2.262	17.13	2	152.244	−54	24.38
0.9917	17.13	2	71.531	67	21.76
0.4893	17.13	2	36.536	9	20.06
0.2518	17.13	2	19.181	−31	18.93
0.0912	17.13	2	7.048	−57	18.06
0.0312	17.13	2	2.437	−26	17.39
2.952	30.64	2	191.160	100	25.90
0.9917	31.20	2	70.782	73	22.74
0.4893	31.16	2	36.140	31	21.14
0.2518	31.13	2	18.974	−8	20.05
0.0912	31.33	2	6.992	−23	19.01
0.0312	31.40	2	2.412	−19	18.53
2.952	40.64	2	190.117	−41	26.34
2.262	40.40	2	150.155	−48	25.56
0.9917	39.95	2	70.335	33	23.31
0.4893	40.16	2	35.904	30	21.78
0.2518	40.54	2	18.794	−51	20.94
0.0912	40.55	2	6.930	−32	19.88
0.0312	40.44	2	2.384	−29	19.61
			(C) KCl		
3.012	0.1013	2	121.699	4	30.41
2.350	0.1013	2	97.823	16	29.95
1.018	0.1013	2	45.147	46	28.85
0.4432	0.1013	2	20.273	24	28.18
0.2555	0.1013	2	11.840	27	27.82
0.0870	0.1013	2	4.071	−6	27.58
0.0585	0.1013	2	2.756	6	27.30
3.012	10.38	2	120.788	22	30.74
2.350	10.38	2	96.994	−71	30.34
1.018	10.38	2	44.718	−42	29.33
0.4432	10.38	2	20.089	−6	28.67
0.2555	10.38	2	11.722	−1	28.36
0.0870	10.38	2	4.075	30	27.62
0.0585	10.38	3	2.749	21	27.51
3.012	17.13	2	120.225	−23	30.95
2.350	17.13	2	96.624	−25	30.52
1.018	17.13	2	44.548	−19	29.54
0.4432	17.13	2	20.001	−6	28.91
0.2555	17.13	2	11.679	7	28.58
0.0870	17.13	2	4.022	−6	28.28
0.0585	17.13	2	2.708	−8	28.26
3.012	31.54	2	119.473	84	31.23
2.350	31.61	2	96.018	66	30.83
1.018	31.61	2	44.219	−18	29.93
0.4432	31.61	2	19.856	0	29.32
0.2555	31.47	2	11.558	−25	29.14
0.0870	31.47	2	3.990	−6	28.74
0.0585	31.47	2	2.684	−11	28.76
3.012	40.26	2	118.945	−87	31.42
2.350	40.51	2	95.673	18	31.00
1.018	40.64	2	44.125	36	30.06
0.4432	40.09	2	19.767	−23	29.56
0.2555	40.02	2	11.511	−32	29.37
0.0870	39.92	2	3.973	−10	28.99
0.0585	39.82	2	2.686	0	28.79
			(D) NaBr		
4.972	0.1013	4	330.637	8	27.26
3.013	0.1013	3	213.208	19	26.38
2.006	0.1013	2	146.617	34	25.86
1.004	0.1013	2	76.003	73	25.13
0.5017	0.1013	2	38.677	−2	24.69
0.2507	0.1013	2	19.543	−4	24.30
0.1003	0.1013	2	7.897	11	23.81
0.0500	0.1013	2	3.960	14	23.43
4.972	10.38	3	329.183	−38	27.64
3.013	10.38	3	212.267	−32	26.82
2.006	10.38	2	145.871	−104	26.38
1.004	10.38	2	75.639	24	25.69
0.5017	10.38	2	38.474	−44	25.31
0.2507	10.38	2	19.446	−19	24.92
0.1003	10.38	2	7.859	6	24.43
0.0500	10.38	2	3.949	20	23.91
4.972	17.13	2	328.591	27	27.83
3.013	17.13	2	211.888	12	27.04
2.006	17.13	2	145.617	−66	26.62
1.004	17.13	2	75.486	24	25.97
0.5017	17.13	2	38.404	−36	25.59
0.2507	17.13	2	19.434	9	25.12
0.1003	17.13	2	7.846	9	24.72
0.0500	17.13	2	3.954	33	23.97
4.972	31.20	2	327.938	59	28.11
3.013	31.13	2	211.498	86	27.36
2.006	31.13	2	145.380	28	26.96
1.004	30.99	3	75.309	26	26.40
0.5017	31.13	2	38.345	0	25.99
0.2507	31.13	2	19.380	4	25.63
0.1003	31.13	2	7.839	22	25.09
0.0500	31.13	2	3.926	15	24.83
4.972	40.07	2	327.874	−47	28.22
0.013	39.88	2	211.360	−43	27.52
2.006	39.99	2	145.342	9	27.11
1.004	39.95	3	75.273	9	26.59

Table I (Continued)

m/(mol kg^{-1})	P, MPa	n^a	$10^3(\Delta\rho)$/(g cm^{-3})	Δb/ppm	$\phi_v{}^c$/(cm^3 mol^{-1})
0.5017	40.09	2	38.292	−41	26.26
0.2507	40.07	2	19.344	−25	25.95
0.1003	40.04	2	7.805	−8	25.61
0.0500	40.06	2	3.928	19	24.98
			(E) LiCl		
4.974	0.1013	2	100.045	−2	20.25
2.977	0.1013	2	64.506	45	19.46
2.015	0.1013	2	45.300	3	19.04
1.004	0.1013	2	23.544	−5	18.48
0.5019	0.1013	2	12.078	0	18.09
0.2506	0.1013	2	6.126	1	17.82
0.0999	0.1013	2	2.490	18	17.40
0.0502	0.1013	2	1.258	9	17.29
4.974	10.38	2	98.591	−34	20.54
2.977	10.38	2	63.503	1	19.80
2.015	10.38	2	44.574	−30	19.41
1.004	10.38	2	23.140	−33	18.90
0.5019	10.38	2	11.881	1	18.51
0.2506	10.38	2	6.020	−3	18.27
0.0999	10.38	2	2.449	19	17.85
0.0502	10.38	2	1.234	6	17.80
4.974	17.13	2	97.849	15	20.69
2.977	17.13	2	62.966	8	19.99
2.015	17.13	2	44.183	−23	19.61
1.004	17.13	2	22.934	−21	19.12
0.5019	17.13	2	11.779	15	18.73
0.2506	17.13	2	5.961	−1	18.52
0.0999	17.13	2	2.422	17	18.13
0.0502	17.13	2	1.227	12	17.96
4.974	31.47	2	96.564	29	20.94
2.977	31.47	2	62.064	34	20.29
2.015	31.40	2	43.502	−17	19.95
1.004	31.40	2	22.570	−1	19.49
0.5019	31.14	3	11.566	6	19.17
0.2506	31.21	2	5.881	26	18.86
0.0999	31.27	2	2.385	25	18.53
0.0502	31.27	2	1.201	9	18.50
4.974	40.20	2	95.975	−21	21.05
2.977	40.42	2	61.584	−23	20.44
2.015	39.99	2	43.193	−12	20.11
1.004	40.02	2	22.381	−8	19.68
0.5019	40.16	2	11.473	17	19.36
0.2506	40.23	2	5.834	34	19.06
0.0999	40.09	2	2.356	18	18.83
0.0502	40.26	2	1.195	15	18.64
			(F) $CaCl_2$		
4.980	0.1013	3	344.431	−35	31.02
3.017	0.1013	2	229.962	−90	28.15
2.006	0.1013	2	161.168	68	26.25
1.005	0.1013	3	85.422	80	23.77
0.5026	0.1013	2	44.217	101	21.85
0.2515	0.1013	3	22.535	6	20.71
0.1010	0.1013	2	9.164	−30	19.86
0.0505	0.1013	2	4.607	−24	19.46
4.980	10.38	2	342.190	72	31.54
3.017	10.38	2	228.325	−103	28.80
2.006	10.38	2	159.940	7	27.02
1.005	10.38	2	84.666	−35	24.74
0.5026	10.38	2	43.790	14	22.96
0.2515	10.38	2	22.323	−29	21.85
0.1010	10.38	2	9.084	−36	20.97
0.0505	10.38	2	4.584	−10	20.24
4.980	17.13	2	341.014	111	31.83
3.017	17.13	2	227.473	−87	29.16
2.006	17.13	2	159.357	58	27.42
1.005	17.13	2	84.318	−29	25.22
0.5026	17.13	2	43.586	1	23.53
0.2515	17.13	2	22.216	−36	22.45
0.1010	17.13	2	9.058	−20	21.42
0.0505	17.13	2	4.560	−13	20.91
4.980	31.29	2	339.029	−177	32.32
3.017	31.30	2	226.338	84	29.72
2.006	31.20	2	158.315	−1	28.14
1.005	31.20	2	83.765	−13	26.05
0.5026	31.23	2	43.227	−46	24.56
0.2515	31.27	2	22.016	−69	23.60
0.1010	31.23	2	8.979	−29	22.58
0.0505	31.20	2	4.518	−19	22.13
4.980	40.71	2	338.787	75	32.46
3.017	40.51	2	225.837	59	29.99
2.006	40.30	2	157.955	32	28.46
1.005	40.64	2	83.484	−40	26.50
0.2515	40.20	2	21.971	−39	23.99
0.1010	40.51	2	8.949	−26	23.11
0.0505	40.64	2	4.505	−14	22.63

[a] n is the number of duplicate runs. [b] $\Delta = (\Delta\rho - \Delta\rho(\text{calcd})) \times 10^6$/g (g cm^{-3}). [c] The ϕ_v's were calculated by using the equation of state of Harr, Gallagher, and Kell for ρ_0.

Table II. Coefficients for Eq 1

salt	$10a$	10^3b	10^4c	10^5d/MPa	10^6e/MPa	10^7f/MPa^2	std error of fit × 10^6/(g cm^{-3})
NaCl	4.2111 (88)[a]	−2.291 (98)	−6.25 (28)	−4.19 (19)	6.99 (82)	1.55 (23)	41.0
$MgCl_2$	8.1726 (245)	−7.883 (359)	−7.19 (133)	−9.20 (58)	22.4 (32)	3.22 (60)	63.1
KCl	4.7557 (133)	−1.982 (190)	−12.32 (70)	−3.90 (31)	3.57 (173)	2.68 (35)	36.6
NaBr	7.9511 (96)	−2.272 (104)	−15.97 (28)	−3.78 (20)	2.40 (82)	4.69 (25)	39.8
LiCl	2.5201 (44)	−1.283 (49)	−4.47 (14)	−4.60 (10)	6.98 (40)	2.52 (12)	20.5
$CaCl_2$	9.3218 (166)	−6.219 (187)	−20.41 (52)	−8.12 (36)	13.1 (15)	5.75 (45)	50.7

[a] The number in parentheses is the 95% confidence limit of each coefficient expressed as an uncertainty in the least significant digit.

from our calculated values by 450 ppm at 0.46 mol kg^{-1} to 20 000 ppm at 4.83 mol kg^{-1}. Comparison with the atmospheric pressure results of Alekhim et al. (*8*) indicates agreement within the errors of their data (Figure 1P). A comparison with their high-pressure results, which requires an extrapolation of our fit to 55 MPa, also demonstrates reasonable agreement (within 0.3% of $\Delta\rho$).

We can compare our results with the experimental adiabatic compressibilities if we assume that the relative adiabatic compressibilities as calculated by Millero and co-workers (*11*, *12*) are equal to the relative isothermal compressibility and are independent of pressure. Appropriate integrations allow for the calculation of the density of the solutions at any pressure. For all salts, except NaCl above 2.0 mol kg^{-1}, the agreement between the densities calculated in this fashion and those generated from the fit is quite good. The calculated density for 5.0 mol kg^{-1} NaCl was 600 ppm low at 5.0 mol kg^{-1} and 40 MPa with no explanation for this difference.

This work adds to an ever-growing list of high-pressure, room-temperature volume data by extending the concentration ranges to 5.0 mol kg^{-1} (3.0 mol kg^{-1} for $MgCl_2$ and KCl) up to pressures of 40 MPa. Empirical equations which are simple in form and which fit the data to within 40 ppm or 0.1% of $\Delta\rho$ are also provided. The comparison of these fitted equations with other available literature data demonstrates that the stated errors of the fits are, in fact, reasonable. In addition, representation of the data as a fit of Δd (as opposed to apparent molar volumes) provides a fit which more realistically approx-

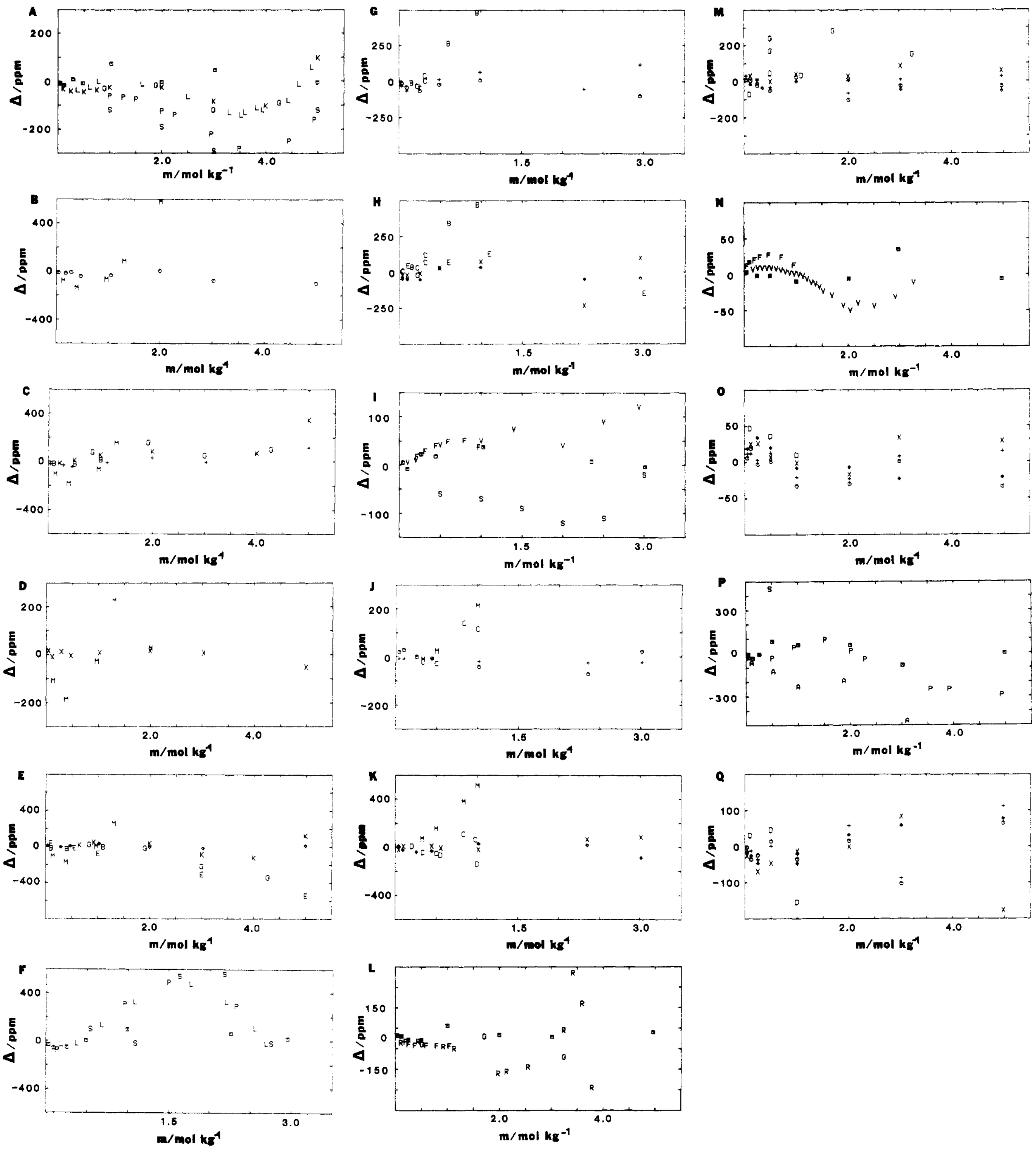

Figure 1. Graphs A–Q are plots of $\Delta = [\Delta\rho(\text{exptl}) - \Delta\rho(\text{calcd})] \times 10^6/(\text{g cm}^{-3})$ vs. molality and $\Delta\rho$ is calculated by eq 1 with the coefficients in Table II for which the following internal symbols apply: (⊡) this work, 0.1013 MPa; (◎) this work, 10 MPa; (+) this work, 17 MPa; (×) this work, 30 MPa; (◊) this work, 40 MPa; (A) Alekhin et al. (*8*); (B) Chen and Millero (*13*); (C) Chen et al. (*10*); (D) Millero et al. (*11*); (E) Millero et al. (*12*); (F) Fortier et al. (*4*); (G) Gibson and Loeffler (*6*); (K) Rogers and Pitzer fit (*9*); (L) LoSurdo et al. (*2*); (M) Chen et al. fit (*10*); (P) Perron et al. (*1*); (R) Robison and Weston (*6*); (S) Romankiw and Chou (*3*); (V) Vaslow (*5*). The salt and pressure (range) pertaining to each graph are as follows:

graph	salt	press./MPa	graph	salt	press./MPa	graph	salt	press./MPa	graph	salt	press./MPa
A	NaCl	0.1013	F	$MgCl_2$	0.1013	J	KCl	10-20	N	LiCl	0.1013
B	NaCl	5-15	G	$MgCl_2$	10-20	K	KCl	30-40	O	LiCl	10-40
C	NaCl	15-25	H	$MgCl_2$	30-40	L	NaBr	0.1013	P	$CaCl_2$	0.1013
D	NaCl	25-35	I	KCl	0.1013	M	NaBr	10-50	Q	$CaCl_2$	10-40
E	NaCl	35-50									

imates experimental errors of vibrating tube densimeters.

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Registry No. NaCl, 7647-14-5; $MgCl_2$, 7786-30-3; KCl, 7447-40-7; NaBr, 7647-15-6; LiCl, 7447-41-8; $CaCl_2$, 10043-52-4.

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Structure of Melts in Binary Organic Eutectics and Molecular Complexes. Phenanthrene–Picric Acid and Anthracene–Picric Acid Systems

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Phenanthrene–picric acid and anthracene–picric acid systems were chosen for detailed thermochemical measurements. Phase-diagram studies confirmed that a maximum is surrounded by two eutectics, and a molecular complex of 1:1 stoichiometry with congruent melting is formed in both systems. Enthalpy of fusion values do not obey the mixture law. The exothermic mixing confirms the compound formation in both systems. The values of enthalpy of mixing for the eutectics show the tendency of ordering in the melts.

Introduction

There has been a great deal of discussion (*1–3*) concerning the nature of liquid eutectics. Three types of structures have been suggested depending on the sign and magnitude of the enthalpy of mixing. Strong interactions between unlike molecules are expected when the enthalpy of mixing is negative. Quasieutectic structures are suggested for the positive enthalpy of mixing. The small departure from the mixture law shows the formation of simple molecular solution. Various types of studies such as viscosity measurements, X-ray scattering, centrifuge, and other structure-related properties have given (*4*, *5*) diverse views. Recently, Singh and Singh (*3*) have measured the heats of fusion for various simple eutectics and found that clustering of parent components is very likely in the eutectic melts. Phenanthrene and anthracene are very similar in structure and both form congruent types of eutectics with picric acid. We carried out detailed experimentation to determine the phase diagram and heats of fusion to throw light on the nature of liquid eutectics and 1:1 molecular complexes.

Table I. Values of Enthalpy of Mixing for Anthracene–Picric Acid and Phenanthrene–Picric Acid Systems

	enthalpy of mixing, kJ mol^{-1}		
system	eutectic 1	eutectic 2	1:1 molecular complex
anthracene–picric acid	−3.98	−1.81	−14.14
phenanthrene–picric acid	−0.54	−2.63	−7.63

Experimental Section

The purification process has been reported in ref *6*. The details of phase-diagram studies are also given in the same paper.

Enthalpy of fusion measurements were carried out on a Perkin-Elmer DSC-2 with a computer-aided data acquisition and

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