where ${}_m\gamma$ is the transfer activity coefficient (medium effect) and subscripts w and s denote aqueous and nonaqueous solvent, respectively. A transfer activity coefficient is a measure of the difference between the free energy of the electrolyte in the given nonaqueous medium and in water; a positive value of log ${}_m\gamma$ indicates that the electrolyte is more favorably solvated in water than in the nonaqueous solvent. This is in fact observed for KPi throughout the methanol–water range. However, both $KBPh_4$ and Ph_4PPi have negative values of log ${}_m\gamma$, indicating more favorable solvation (lower free energy) in the nonaqueous media than in water. This is to be expected since the large polarizable tetraphenyl ions are strongly solvated via dispersion interactions by the more polarizable methanol molecules. In general, the trends in solubilities and transfer activity coefficients observed here for methanol–water solvents parallel those reported by us earlier for ethanol–water solvents (*3*, *7*, *13*).

Glossary

A_{DH}	Debye–Hückel limiting slope
A_1, A_2, A_3	empirical coefficients of power terms of $I^{1/2}$ in eq 4
$a_\pm$	mean ionic activity, mol/L
C	solubility of electrolyte, mol/L
C_0	solubility in pure solvent, mol/L
C_I	solubility in presence of added salt at ionic strength I, mol/L
$f_\pm$	mean ionic activity coefficient of electrolyte, molar scale
$f_{\pm,0}$	mean ionic activity coefficient in absence of added salt
$f_{\pm,I}$	mean ionic activity coefficient in presence of added salt at ionic strength I
I	ionic strength, mol/L
K_A	ion-pair association constant, L/mol
K_s	solubility product of an electrolyte, mol^2/L^2
${}_sK_s$	solubility product in a nonaqueous solvent, mol^2/L^2
${}_wK_s$	solubility product in water, mol^2/L^2
M	mol/L of solution

Greek Letters

α	degree of dissociation into ions
α_0	degree of dissociation into ions in pure solvent
α_I	degree of dissociation in the presence of added salt at ionic strength I
${}_m\gamma$	transfer activity coefficient (medium effect)
${}_m\gamma_\pm$	mean ionic transfer activity coefficient of an electrolyte
ϵ_{max}	maximum molar absorptivity

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Supplementary Material Available: Solubilities of the title electrolytes as a function of LiCl concentration, Tables I, II, and III (11 pages). Ordering information is given on any current masthead page.

Studies of Self-Association in Nonaqueous Solvents by Titration Calorimetry. Halogen-Substituted Acetic and Propionic Acids in Benzene

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A calorimetric enthalpy of dilution technique was used to obtain apparent relative molar enthalpy (ϕ_L) data for the following carboxylic acids in benzene at 25.00 ± 0.07 °C: acetic, chloroacetic, bromoacetic, iodoacetic, propionic, 2-chloropropionic, and 3-chloropropionic. The data are interpreted in terms of a monomer–dimer equilibrium and values of the thermodynamic parameters K, $\Delta H°$, and $\Delta S°$ for dimerization are reported. The effect of small amounts of water in the benzene was studied and it was found to be most pronounced for the acids of greatest aqueous acid strength.

The self-association of carboxylic acids through hydrogen bond formation is known to occur in nonpolar solvents. Equilibrium constants for these associations have been determined by a variety of techniques, among which are infrared spectroscopy, distribution measurements, dielectric constant measurements, and others. Values of $\Delta H°$ and $\Delta S°$ have been reported much less frequently.

A calorimetric enthalpy of dilution technique has been developed (*13*, *15*) by which K as well as $\Delta H°$ for these associations can be determined from measurements carried out at a single temperature. The apparent relative molar enthalpy, ϕ_L, is determined and related to the thermodynamic parameters of association. This technique has been applied to the study of carboxylic acid self-association in nonpolar solvents (*17*–*20*). This paper reports the results of calorimetric investigations of acetic, chloroacetic, bromoacetic, iodoacetic, propionic, 2-chloropropionic, and 3-chloropropionic acids in benzene and of the effects of trace amounts of water on the association reactions.

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Experimental Section

Enthalpy of dilution measurements were made with a Tronac 450 adiabatic titration calorimeter equipped with a 50-mL reaction vessel as previously described (*17*, *18*). The calorimeter was modified to include a Metrohm Herisau piston buret powered by a precision synchronous motor for delivery of solutions to the reaction vessel. The temperature of the calorimeter fluid was maintained at 25.00 ± 0.0002 °C by a Tronac 1040 temperature controller. The temperature within the reaction vessel was 25.00 ± 0.07 °C. Data were recorded on a Sargent-Welch SRG recorder. The calorimeter calibration was checked by titration of imidazole with standard HCl. We obtained $\Delta H^\circ = 8.72$ (±0.04) kcal/mol for the protonation reaction, in excellent agreement with the recommended 8.71 (±0.04) kcal/mol (*16*). Results are reported in terms of the calorie, defined equal to 4.184 J. The calorimeter has a sensitivity of about ±3 cal/mol or ±0.4% in ϕ_L, whichever is greater, as used in the enthalpy of dilution experiments.

All acids used were the best grade readily obtainable and were used without further purification. Acids which appeared to be hygroscopic or were known to contain water were placed over P_2O_5 in a desiccator (*18*). For acids not in the above categories, experiments performed with similarly dried or undried acid gave results that did not differ significantly. Sources and purity are as follows: acetic, Mallinckrodt, reagent grade (99.7%); propionic, Mallinckrodt, reagent grade (99% minimum); chloroacetic, Eastman, mp 62–64 °C; bromoacetic, MCB, mp 46–48 °C; iodoacetic, Baker, Baker grade, mp 80.5–82 °C; 2-chloropropionic, Eastman, bp 82–84 °C (15 mm); 3-chloropropionic, Eastman, mp 40–42 °C.

GC-Spectrophotometric grade benzene, 99.9% pure (Baker), was used to prepare all solutions and for all enthalpy of dilution measurements. The benzene was dried by placing it in vapor contact with P_2O_5 in a desiccator (*3*). Dried benzene placed in the reaction vessel and "titrated" with dried benzene showed no detectable increase in water concentration. Water determinations were by Karl Fischer titration (*18*).

The "titrant" acid solutions contained between 0.25 and 0.6 mol/L of the acid. These solutions were delivered at a constant rate of about 0.4 mL/min to the calorimeter vessel containing 50.00 mL of benzene through a glass coil immersed in the calorimeter bath. Enthalpy of dilution data were recorded continuously (*18*).

Calculations

When an acid solution in benzene (acid concentration F_T) is added to benzene in the reaction vessel, enthalpy of dilution data corresponding to the following processes can be obtained.

$$F_T \rightarrow F_1 \qquad \Delta H_1 \tag{1a}$$

$$F_T \rightarrow F_2 \qquad \Delta H_2 \tag{1b}$$

$$F_T \rightarrow F_i \qquad \Delta H_i \tag{1i}$$

The enthalpy of dilution of the "titrant" acid solution to infinite dilution is

$$F_T \rightarrow 0 \qquad \Delta H_0 = -\phi_{LT} \tag{2}$$

Combination of eq 1 and 2 yields

$$F_1 \rightarrow 0 \qquad -\phi_{L1} = \Delta H_0 - \Delta H_1 \tag{3a}$$

$$F_2 \rightarrow 0 \qquad -\phi_{L2} = \Delta H_0 - \Delta H_2 \tag{3b}$$

$$F_i \rightarrow 0 \qquad -\phi_{Li} = \Delta H_0 - \Delta H_i \tag{3i}$$

The correct value of $-\phi_{LT}$ can be found by extrapolation of a plot of ΔH_i vs. F_i (or F_i^2, etc.) to zero concentration. In practice, however, uncertainties in ΔH_i are large at small F_i, making such an extrapolation uncertain. If the monomer–dimer reaction (or any other monomer–single polymer reaction)

$$2A \rightleftharpoons A_2 \tag{4}$$

is the only equilibrium process occurring in dilute solutions of the carboxylic acid in a dry nonpolar solvent, we are able to avoid this extrapolation by treating ϕ_{LT} as an independent variable.

For the dilution process of eq 3 we can write

$$F_i\phi_{Li} = \Delta H_2^\circ[A_2]_i \tag{5}$$

where ΔH_2° is the standard enthalpy change for reaction 4, assuming that "nonideal" enthalpies of dilution of A_2 and A are zero. Combination of eq 5 with the equilibrium constant expression (assuming activity coefficients are unity)

$$K_2 = [A_2]/[A]^2 \tag{6}$$

and the material balance expression

$$F_i = [A]_i + 2[A_2]_i \tag{7}$$

yields an equation of the form

$$\phi_{Li} = \Delta H_2^\circ/2 + (-\Delta H_2^\circ/4K_2)^{1/2}(-\phi_{Li}/F_i)^{1/2} \tag{8}$$

Plotting ϕ_{Li} vs. $(-\phi_{Li}/F_i)^{1/2}$ gives a straight line of intercept $\Delta H_2^\circ/2$ and slope $(-\Delta H_2^\circ/4K_2)^{1/2}$, from which values of K_2 and ΔH_2° for reaction 4 can be obtained.

A value of ΔH_0 (which is used in eq 3 to obtain values of ϕ_{Li}) which is too small causes a curvature in the plot of eq 8 which is concave upward. A value of ΔH_0 which is too large causes curvature which is concave downward. An iterative technique was used to determine the value of ΔH_0 which produced the smallest standard deviation in a least-squares fit of the data to eq 8 for each dilution experiment.

In order to avoid the necessity of introducing the variable ΔH_0 into the data analysis, an alternate method of calculations was also used. Letting α_i represent the fraction of monomers that is associated at any formal acid concentration, F_i, one obtains

$$K_2 = \alpha_i/[2F_i(1 - \alpha_i)^2] \tag{9}$$

and

$$\phi_{Li} = (\alpha_i/2)\Delta H_2^\circ \tag{10}$$

from eq 5, 6, and 7.

By combining the data from any two acid concentrations, F_i and F_j, one obtains from eq 10

$$\Delta H_2^\circ = 2(\phi_{Li} - \phi_{Lj})/(\alpha_i - \alpha_j) \tag{11}$$

which is equivalent to

$$\Delta H_2^\circ = 2(\Delta H_i - \Delta H_j)/(\alpha_i - \alpha_j) \tag{12}$$

By iterative techniques, a value of K_2 can be found which results in a minimum in the deviation of values of ΔH_2° calculated from all combinations of data in eq 12.

Results

Enthalpy of dilution data were obtained in benzene that had been dried over P_2O_5. The residual water concentration in the benzene was found to be 0.0015 M. Average values of $-\phi_L$ for the acids studied are presented in Table I. Also included in the table are the thermodynamic parameters obtained by a least-squares fit of the data to eq 8, as well as those obtained by application of eq 9–12 to the data.

The thermodynamic functions are summarized in Table II. Values of K_2 and ΔH_2° obtained by the two methods of calculation have been averaged, and values of ΔS_2° have been calculated from the averages. The uncertainties given in the table are our estimates of a 95% confidence interval based on

Table I. Average Values of $-\phi_L$ (cal/mol of acid) for Addition of Carboxylic Acids in Benzene Solvent to 50.00 mL of Benzene Containing 0.0015 M H_2O at 25.00 ± 0.07 °C[a-c]

	F_T									
	acetic			chloroacetic	bromoacetic	iodoacetic	propionic	2-chloropropionic	3-chloropropionic	
mL added	0.4088 M	0.4642 M	0.5492 M	0.4087 M	0.3225 M	0.3773 M	0.5447 M	0.5396 M	0.3568 M	0.5087 M
0.038_9						523			595	
0.097_2				719	519	1007	2009		1142	1387
0.136_1			1862	908	686	1220	2300	987	1376	1630
0.194_5	1965	1974	2138	1146	852	1484	2588	1208	1639	1909
0.233_3	2110				968	1594				
0.291_7	2285	2266	2423	1416	1105	1767	2904	1486	1954	2222
0.330_6	2368				1176	1861				
0.388_9	2485	2460	2618	1620	1290	1986	3110	1683	2161	2432
0.486_1	2638	2608	2762	1785	1443	2150	3256	1832	2323	2592
0.583_4	2758	2725	2869	1915	1565	2278	3375	1957	2449	2715
0.680_6	2856	2818	2962	2019	1661	2389	3465	2058	2554	2817
0.777_8	2939	2897	3036	2110	1755	2483	3543	2141	2645	2903
0.875_0	3011				1834	2557	3611	2218	2725	2974
0.972_3	3073	3022	3154	2261	1905	2635	3669	2282	2793	3039
1.069_5	3124				1968	2701				
1.166_7	3172	3119	3244	2380	2025	2757	3761	2394	2907	3145
1.263_9	3215				2078	2807				
1.361_2	3254	3196	3314	2479	2126	2852	3835	2485	2999	3228
1.555_6	3320	3260	3375	2561	2212	2932	3896	2561	3076	3298
1.750_1	3376	3314	3425	2632	2283	3001	3946	2627	3140	3356
1.944_5	3424	3360	3468	2696	2347	3060	3992	2683	3196	3406
2.139_0	3465	3400	3504		2402	3113	4027	2733	3245	3450
2.333_4	3502	3434	3537		2452	3159	4061	2777	3288	3488
2.527_9	3535	3466	3567		2498	3200	4090	2817	3327	3523
2.722_3	3565	3494	3594		2539	3237	4117	2852	3362	3554
2.916_8	3592	3520	3617		2577		4141	2885	3395	3583
ΔH_0 ($-\phi_{LT}$)	4253	4134	4188	3863	3603	4153	4723	3727	4200	4247
Equation 8										
K_2	440	417	430	159	139	256	554	146	326	322
$-\Delta H_2°$, kcal/mol of dimer	8.98	8.72	8.79	8.46	8.05	8.85	9.84	8.07	8.96	9.04
$-\Delta S_2°$, cal/(K mol of dimer)	18.0	17.3	17.4	18.3	17.2	18.7	20.5	17.2	18.6	18.8
std dev	3.2	4.8	3.0	6.3	5.5	11.1	2.4	2.8	6.5	8.2
Equations 9–12										
K_2	486	508	491	162	146	237	580	150	323	423
$-\Delta H_2°$, kcal/mol of dimer	9.23	9.25	9.13	8.45	8.04	8.84	9.98	8.10	8.94	9.60
$-\Delta S_2°$, cal/(K mol of dimer)	18.7	18.6	18.3	18.2	17.1	18.8	20.8	17.2	18.5	20.2
std dev in $\Delta H_2°$	0.14	0.20	0.15	0.12	0.15	0.17	0.13	0.10	0.12	0.34

[a] Each column is the average of two or three determinations at that concentration. The data for individual runs may be found in ref 18, except for 0.4088 M acetic acid, which is incorrect in ref 18. [b] The average deviation in ϕ_L values from individual determinations (see footnote *a*) at each concentration, averaged over all acids in the table during the dilution is as follows: 0.2 mL added, 88; 1.2 mL added, 108; 2.9 mL added, 117; ΔH_0, 112. [c] Note that the ϕ_L values listed in this table were obtained by constraining the enthalpy data to fit eq 8 as discussed in the Calculations section.

Table II. Thermodynamic Functions for Dimerization of Halogen-Substituted Acetic and Propionic Acids in Benzene Containing 0.0015 M H_2O at 25.00 ± 0.07 °C[a]

acid	K_2[b]	$-\Delta H_2°$, kcal/mol of dimer	$-\Delta S_2°$,[b] cal/(K mol of dimer)
acetic	462 ± 108	9.02 ± 0.95	18.1 ± 2.7
chloroacetic	160 ± 29	8.46 ± 0.43	18.3 ± 1.1
bromoacetic	142 ± 40	8.04 ± 0.94	17.1 ± 2.6
iodoacetic	246 ± 58	8.84 ± 0.56	18.7 ± 1.3
propionic	567 ± 104	9.91 ± 0.54	20.6 ± 1.5
2-chloropropionic	148 ± 22	8.08 ± 0.4	17.2 ± 1
3-chloropropionic	348 ± 85	9.14 ± 0.53	19.0 ± 1.5

[a] Uncertainty intervals are our estimate of the 95% confidence interval. See text for discussion (*18*). [b] On the basis of molar concentration scale standard states.

reproducibility and other factors. (For a more detailed discussion of uncertainties see ref 18.)

To examine the effect of the presence of water on the data, several of the acids were studied in benzene containing 0.0053 M H_2O. These results are presented in Table III, and the thermodynamic functions are averaged and summarized in Table IV.

Inspection of the values of the standard deviation of the fit of the data to eq 8 in Tables I and III indicates that the monomer–dimer model is sufficient to describe the enthalpy data well within the limits of experimental error of the calorimetric measurements (≥±0.4%). See also footnote *b* in Tables I and III. Consequently, the data in Tables I and III do not justify the consideration of polymers and dimers (*14*, *18*). It is also easily verified that any monomer–single polymer model other than the monomer–dimer model is not in agreement with the data (*14*, *18*).

Comparison of Table II and Table IV indicates that the values of K_2 and $\Delta H_2°$ for the dimerization of acetic and propionic acids are not affected significantly by increasing the water concentration to 0.0053 M. [At higher water concentrations not reported here the apparent value of $\Delta H_2°$ became less negative (*18*).] For the halogen-substituted acetic acids, however, a significant decrease in the magnitude of $\Delta H_2°$ is seen, and a small but perhaps significant decrease in K_2 is also observed with increasing water concentration.

It has been postulated that the hydration of carboxylic acids in benzene increases with increasing aqueous acidity (*1*). Also, it has been shown that dimerization decreases with increasing aqueous acididty (*5*). The results reported here are consistent

Table III. Average Values of $-\phi_L$ (cal/mol of acid) for Addition of Carboxylic Acids in Benzene Solvent to 50.00 mL of Benzene Containing 0.0053 M H_2O at 25.00 ± 0.07 °C[a-c]

	F_T											
	acetic			chloroacetic			bromoacetic		iodoacetic		propionic	
mL added	0.3712 M	0.4081 M	0.5413 M	0.2717 M	0.3055 M	0.3827 M	0.3709 M	0.4698 M	0.3090 M	0.4613 M	0.4316 M	0.5022 M
0.038_9		799										
0.097_2	1260	1389				563						1739
0.136_1	1493	1664		515	530	712				973		2012
0.194_5	1760	1928	2400	669	677	902	827	964		1180	2601	2296
0.233_3				740	775		902	1083	1023	1309	2750	
0.291_7	2057	2242	2700	858	871	1145	1035	1189	1165	1456	2933	2602
0.330_6				926	946		1108	1278	1234	1547	3034	
0.388_9	2287	2443	2906	1020	1050	1317	1204	1385	1355	1646	3157	2807
0.486_1	2435	2601	3058	1154	1178	1456	1338	1533	1504	1793	3316	2957
0.583_4	2558	2723	3174	1260	1287	1572	1457	1648	1614	1911	3438	3069
0.680_6	2665	2823	3268	1355	1384	1668	1554	1745	1713	2011	3537	3163
0.777_8	2749	2909	3347	1438	1464	1754	1640	1827	1792	2096	3618	3243
0.875_0	2822	2983		1510	1541		1714	1898	1862	2171	3686	3309
0.972_3	2886	3045	3474	1569	1610	1895	1780	1962	1928	2236	3748	3368
1.069_5				1628	1670		1842	2020	1986	2295	3800	
1.166_7	2990	3153	3569	1681	1725	2008	1895	2074	2039	2345	3848	3463
1.263_9				1732	1778		1943	2120	2088	2390	3891	
1.361_2	3083	3236	3645	1779	1825	2096	1989	2162	2129	2433	3928	3540
1.555_6	3154	3306	3706	1859	1904	2172	2065	2236	2211	2507	3993	3603
1.750_1	3214	3363	3758	1931	1975	2238	2133	2305	2281	2570	4047	3656
1.944_5	3266	3413	3804	1993	2036	2296	2191		2341	2610	4092	3701
2.139_0	3310	3458	3844	2049	2091	2348	2244		2392		4136	3740
2.333_4	3350		3878	2099	2141	2393	2291		2438		4171	3775
2.527_9	3385		3909	2144	2186	2434	2333		2479		4204	3805
2.722_3	3417		3937	2185					2517		4232	3833
2.916_8	3446		3962	2223								3859
$\Delta H_0(-\phi_{LT})$	4163	4290	4560	3249	3303	3425	3340	3433	3450	3613	4904	4453
Equation 8												
K_2	382	409	481	127	115	139	124	127	177	175	632	487
$-\Delta H_2°$, kcal/mol of dimer	8.86	9.04	9.54	7.34	7.46	7.54	7.45	7.53	7.62	7.84	10.22	9.34
$\Delta S_2°$, cal/(K mol of dimer)	17.9	18.4	19.7	15.0	15.6	15.5	15.4	15.6	15.3	16.0	21.5	19.0
std dev	5.5	6.5	4.0	5.7	5.7	2.6	6.6	5.7	7.0	5.2	3.2	4.1
Equations 9–12												
K_2	419	402	543	133	120	139	134	130	192	178	574	567
$-\Delta H_2°$, kcal/mol of dimer	9.02	9.04	9.92	7.33	7.48	7.54	7.48	7.55	7.68	7.86	9.93	9.73
$-\Delta S_2°$, cal/(K mol of dimer)	18.3	18.4	20.8	14.9	15.6	15.5	15.4	15.7	15.3	16.1	20.7	20.0
std dev in $\Delta H_2°$	0.20	0.14	0.19	0.20	0.20	0.07	0.20	0.23	0.23	0.22	0.11	0.23

[a] See footnote *a*, Table I. [b] See footnote *b*, Table I: 0.2 mL added, 70; 1.2 mL added, 88; ΔH_0, 92. [c] See footnote *c*, Table I.

Table IV. Thermodynamic Functions for Dimerization of Halogen-Substituted Acetic and Propionic Acids in Benzene Containing 0.0053 M H_2O at 25.00 ± 0.07 °C[a]

acid	K_2[b]	$-\Delta H_2°$, kcal/mol of dimer	$-\Delta S_2°$,[b] cal/(K mol of dimer)
acetic	439 ± 119	9.24 ± 0.79	18.9 ± 2.2
chloroacetic	129 ± 27	7.45 ± 0.59	15.3 ± 1.7
bromoacetic	129 ± 22	7.50 ± 0.43	15.5 ± 1.2
iodoacetic	180 ± 27	7.60 ± 0.39	15.2 ± 1.1
propionic	565 ± 104	9.80 ± 0.54	20.3 ± 1.5

[a] Uncertainty intervals are our estimate of the 95% confidence interval. See text for discussion (*18*). [b] On the basis of molar concentration scale standard states.

with the idea that the more acidic acids interact with water to a greater extent than the less acidic ones. For some acids, then, particularly the stronger ones, the presence of water in the solvent may be important even at very low water concentration.

It is evident from Table II that substituent groups have an effect on the dimerization constant. The positive inductive effect of the methyl group results in a small increase in K_2 for propionic acid, while the negative inductive effect of the halogens lowers K_2. This is consistent with the effect of these same substituent groups on aqueous acidity (*5*).

The enthalpy of dimerization is not as sensitive to substituent effects (*7*). The results reported here tend to support that conclusion although the magnitudes of the uncertainties and the effect of water make a conclusive argument impossible.

Literature values for the dimerization constant of acetic acid in benzene at 25 °C range from 130 (*4*) to 832 (*6*). A value of 500 has been reported (*2*), as well as values of 500 at 28 °C (*11*) and 375 at 30 °C (*10*), which compare favorably with the results reported here. Values of $\Delta H_2°$ from −8.19 kcal/mol (*4*) to −9.70 kcal/mol (*8*) have been reported.

A value of K_2 for propionic acid of 162 has been reported (*4*). Using our K_2 and $\Delta H_2°$ values from Table II in the van't Hoff equation, we calculate K_2 = 430 at 30 °C, in good agreement with a reported K_2 = 390 (*10*). For chloroacetic acid, values of 24 at 20 °C (*9*), 48 at 25 °C (*12*), and 102 at 30 °C (*10*) have been reported. Comparisons for the other acids reported here are lacking in the literature.

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Ethylene Solubility and Diffusivity in Hexane–Dodecane and Ethylene Glycol–Butanol Solutions

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Densities, refractive indices, viscosities, ethylene solubilities, and diffusion coefficients all at 25 °C are reported for the solvent solutions composed of hexane–dodecane and butanol–ethylene glycol. In the first of these two solvent solutions both components were nonpolar whereas in the second both were polar and expected to form hydrogen-bonding association complexes in solution. A comparison of the various solution properties for these two types of solutions was found useful. The data were also compared with previously reported results when available and predicted values utilizing empirical equations when applicable.

Introduction

A knowledge of the solution properties for mixed solvents of two (or more) components is frequently required in the chemical processing industry. These properties may include the density, viscosity, or gas solubility and diffusivity, as well as refractive index for possible solution analysis, among others. Relatively few data are available for gas solubilities and diffusion coefficients in mixed solvents. In this work the above-mentioned solution properties, as well as ethylene solubilities and diffusivities are reported at 25 °C both for nonpolar solvent solutions composed of hexane and dodecane and for solutions composed of the polar liquids butanol and ethylene glycol.

The subject of liquid diffusion in nonelectrolytes has been extensively reviewed in two parts by Ghai et al. (*9*, *10*) with regard to most aspects of diffusion including measurement techniques, theoretical considerations, and predictive equations. The particular subject of diffusivities of dissolved gases was reviewed earlier by Himmelblau (*17*). The Wilke–Chang relation (*32*) for predicting diffusivities in liquids including those for dissolved gases has stood the test of time, although two significant limitations for its use have been observed by Akgerman and Gainer (*1*). Diffusivities of small solute gas molecules were not usually accurately predicted nor were those involving solvents whose viscosities were greater than 3–5 cP. The latter authors developed a correlation (*1*, *2*) for diffusivities of dissolved gases based on the absolute rate theory which they showed to be a significant improvement over the Wilke–Chang correlation although also more complex:

$$D_{AB} = \frac{kT}{\xi_A \mu_B}\left(\frac{N}{V_B}\right)^{1/3}\left(\frac{M_B}{M_A}\right)^{1/2} \exp\left(\frac{E_{\mu B} - E_{DAB}}{RT}\right) \quad (1)$$

$$E_{\mu B} - E_{DAB} = E_{BB}^{j}\{1 - (E_{AA}^{j}/E_{BB}^{j})^{1/(\xi_A+1)}\} \quad (2)$$

$$\xi_A = 6(V_A/V_B)^{1/6} \quad (3)$$

The work of the original authors should be consulted for methods of calculating the various activation energies and other parameters.

The diffusivity of a gas in a mixed solvent solution composed of two liquids may be considered to involve a pseudobinary system since the gas component is usually very dilute. A number of methods have been proposed to describe the diffusivity of a dilute species in mixed solvents as discussed by Himmelblau in his review (*17*). More recently Tang and Himmelblau (*28*) and Leffler and Cullinan (*20*) have addressed this problem. Several possible relations were described by the former authors, none of which was clearly superior in representing the diffusivity of toluene and CO_2 in several mixed solvent solutions; however, the relation best able to represent the data is as follows:

$$D_{1M}(\eta_M)^{1/2} = x_2 D_{12}(\eta_2)^{1/2} + x_3 D_{13}(\eta_3)^{1/2} \quad (4)$$

From a basis of the Vignes equation (*31*) Leffler and Cullinan developed an equation for the concentration dependence of the diffusivity of a dilute species in a mixture of two solvents as follows:

$$\lim_{x_1 \to 0} (D_{1M})\, \eta = (D^{\circ}{}_{12}\eta_2)^{x_2}(D^{\circ}{}_{13}\eta_3)^{x_3} \quad (5)$$

Equation 5 was not specifically tested for gaseous solutes nor for highly polar solvent mixtures; hence its application to such systems is uncertain. An empirical expression for the relation between diffusivity of a dilute solute in a number of solvents or mixed solvent solutions was reported by Hayduk and Cheng (*14*).

$$D^{\circ}{}_{AB}\eta^{A} = B \quad (6)$$

Equation 6 could be applied to gaseous solutes but was not expected to apply when the solvents or solvent solutions were strongly associating.

Other properties which are usually required for the determination and correlation of gas diffusivities in mixed solvents include the gas solubility, solution viscosity and density for the solvent solutions. In addition it is necessary to have a method of analysis for the solvent compositions, usually by means of refractive index measurements. Theoretical aspects of gas solubilities in mixed solvents have been recently discussed by