Densities and Refractive Indices of Aqueous Mixtures of Alkoxy Alcohols

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Densities and refractive indices of aqueous mixtures of alkoxy alcohols were measured at 25 °C as a function of composition. The data obtained were utilized to test refractive index mixture rules. It is found that the Lorentz–Lorenz and Gladstone–Dale equations perform considerably well within the experimental accuracy in those systems.

Introduction

Densities and refractive indices of aqueous mixtures of alkoxy alcohols, which are widely used as good solvents for lacquer, were measured as a function of composition. The Lorentz–Lorenz,[1] the Wiener,[2] the Heller,[3] the Gladstone–Dale,[4] and the Arago–Biot[5] equations, which are the most important refractive index mixture rules used for determining the refractive index of a solution, are scrutinized regarding their performance in those systems by using the data obtained.

Experimental Section

Materials. Water used was prepared by distilling deionized water with an all-Pyrex still of special design.[6] The special grades of 2-methoxyethanol (MeOEtOH) and 2-ethoxyethanol (EtOEtOH) were obtained from Wako Chemical Co. The extra pure grade of 2-propoxyethanol (PrOEtOH), 2-isopropoxyethanol (i-PrOEtOH) and 2-butoxyethanol (BuOEtOH) were obtained from Tokyo Kasei Co. All these compounds were fractionally distilled under reduced pressure through a fractionating column before use. 3-Methoxy-1-propanol (MeOPrOH) and 3-ethoxy-1-propanol (EtOPrOH) were synthesized and purified according to the method of Smith and Sprung.[7] The method of Cretcher and Pittenger[8] was adopted to synthesize 2-isobutoxyethanol (i-BuOEtOH). The purity of all these compounds was confirmed to be more than 99.9 wt % with gas chromatography.

Instrumental Section. Refractive indices were measured at 25 °C with an Atago 301 Abbe refractometer of which the index accuracy was ±0.0002. The temperature consistency of the refractometer was controlled within ±0.1 °C by circulating water through it from a constant-temperature water bath. Densities were measured with a Shibayama Kagaku Digital Density Meter SS-D 200 at 25 ± 0.01 °C. The basic principle of this instrument is similar to that of the Anton Paar K. G.,[9] that is, to measure the variation of the natural frequency of a U-shaped hollow oscillator when filled with liquids of different density. Introduction of each liquid of different density changes the natural frequency or the period of the oscillator. In actual measurements, the time lapse, T, during a preset number of periods is measured by a crystal-controlled timer.

The density of the unknown liquid, ρ_1, is measured by a reference to that of a known standard, ρ_2. The difference between the densities of the samples is given by

$$\rho_1 - \rho_2 = (1/A)(T_1^2 - T_2^2) \tag{1}$$

where T_1 and T_2 are the time lapse measured, respectively. The constant A is an instrument constant and is obtained from calibration measurements with samples of known density. In the present studies, the reference samples used for calibration were pure water and air.

The difficulty was found in maintaining the temperature consistency of the density meter within ±0.01 °C by circulating water through it from a constant-temperature water bath. Thus, the sample cell was directly installed in the water bath of which temperature was controlled within ±0.01 °C. The mixtures investigated were prepared by weight. The accuracy of the mass fraction is ±1 × 10⁻⁴. The probable error in the density of the sample solutions is ±1 × 10⁻⁴ g/cm³. The density and the refractive index of the i-BuOEtOH–H₂O system were measured at 20 ± 0.01 °C, because this system has lower critical solution temperature near 25 °C. All the above measurements were carried out in a constant-temperature room of 25 ± 1 °C.

Results and Discussion

The densities and refractive indices of the mixtures have been tabulated in Tables I–VIII and have been plotted against the composition in Figures 1 and 2, respectively. The refractive index mixture rules discussed are given as

the Lorentz–Lorenz equation[1]

$$\left(\frac{n_{12}^2 - 1}{n_{12}^2 + 2}\right)\frac{1}{\rho_{12}} = \left(\frac{n_1^2 - 1}{n_1^2 + 2}\right)\frac{p_1}{\rho_1} + \left(\frac{n_2^2 - 1}{n_2^2 + 2}\right)\frac{p_2}{\rho_2} \tag{2}$$

the Wiener equation[2]

$$\frac{n_{12}^2 - n_1^2}{n_{12}^2 + 2n_1^2} = \phi_2 \frac{n_2^2 - n_1^2}{n_2^2 + 2n_1^2} \tag{3}$$

the Heller equation[3]

$$\frac{n_{12} - n_1}{n_1} = \frac{3}{2}\phi_2\left(\frac{m^2 - 1}{m^2 + 2}\right) \tag{4}$$

the Gladstone–Dale equation[4]

$$\frac{n_{12} - 1}{\rho_{12}} = \left(\frac{n_1 - 1}{\rho_1}\right)p_1 + \left(\frac{n_2 - 1}{\rho_2}\right)p_2 \tag{5}$$

the Arago–Biot equation[5]

$$n_{12} = \phi_1 n_1 + \phi_2 n_2 \tag{6}$$

Here, n_{12}, n_1, and n_2 are the refractive indices of solution, solvent, and solute, respectively, ϕ_1 and ϕ_2 are the volume fractions of the respective components in the solution, and $m = n_2/n_1$. The volume fraction ϕ_i can be obtained either from $\phi_i = c_i/\rho_i$, where c_i is the concentration in g/cm³ and ρ_i is the density of the ith component, or from $\phi_i = p_i\rho_{ij}/\rho_i$, where p_i is the weight fraction of the ith component and ρ_{ij} is the density of the mixture of the two compounds. Equations 3 and 4 can be strictly valid only in the case of volume additivity, i.e., no volume expansion or contraction during mixing of the pure components. These equations take the following forms:[10]

$$n_{12} = \left(\frac{2A + 1}{1 - A}\right)^{1/2} \tag{2a}$$

Table I. Mixtures of H_2O (1) and MeOEtOH (2)[a]

p_2, wt %	ρ_{12},[b] g/cm^3	n_{12} obsd[c]	ΔV,[d] cm^3	$\Delta n = n_{12}$ obsd $- n_{12}$ calcd[e]						
				eq 2a	eq 2a*	eq 3a*	eq 4a*	eq 5a	eq 6a	eq 5a* and 6a*
100	0.9605	1.4002	0	0	0	0	0.0006	0	0	0
88.49	0.9769	1.3972	−0.0131	−0.0010	0.0039	0.0038	0.0043	−0.0006	−0.0134	0.0037
77.71	0.9888	1.3931	−0.0213	−0.0014	0.0067	0.0065	0.0069	−0.0007	−0.0218	0.0064
67.42	0.9972	1.3877	−0.0259	−0.0017	0.0081	0.0078	0.0082	−0.0009	−0.0268	0.0077
57.46	1.0029	1.3817	−0.0278	−0.0017	0.0089	0.0086	0.0088	−0.0008	−0.0288	0.0085
47.73	1.0061	1.3745	−0.0272	−0.0019	0.0084	0.0081	0.0083	−0.0011	−0.0285	0.0080
38.16	1.0068	1.3667	−0.0242	−0.0018	0.0073	0.0071	0.0072	−0.0012	−0.0257	0.0087
28.67	1.0051	1.3532	−0.0189	−0.0016	0.0055	0.0053	0.0054	−0.0012	−0.0203	0.0052
19.19	1.0022	1.3498	−0.0124	−0.0009	0.0038	0.0036	0.0036	−0.0007	−0.0132	0.0035
9.61	0.9993	1.3411	−0.0059	−0.0005	0.0017	0.0016	0.0016	−0.0004	−0.0064	0.0015
0	0.9970	1.3328	0	0	0	0	0	0	0	0

[a] Data apply to the sodium D line and temperature of 25 ± 0.01 °C. [b] Observed density. [c] Observed refractive index. [d] Volume change on mixing calculated from eq 7. [e] Refractive index calculated by using eq 2a–6a*.

Table II. Mixtures of H_2O (1) and EtOEtOH (2)[a]

p_2, wt %	ρ_{12},[b] g/cm^3	n_{12} obsd[c]	ΔV,[d] cm^3	$\Delta n = n_{12}$ obsd $- n_{12}$ calcd[e]						
				eq 2a	eq 2a*	eq 3a*	eq 4a*	eq 5a	eq 6a	eq 5a* and 6a*
100	0.9286	1.4060	0	0	0	0	0.0007	0	0	0
87.95	0.9488	1.4026	−0.0140	−0.0009	0.0043	0.0042	0.0046	−0.0013	−0.0137	0.0040
77.09	0.9644	1.3985	−0.0230	−0.0011	0.0075	0.0073	0.0076	−0.0013	−0.0225	0.0071
66.98	0.9762	1.3972	−0.0281	−0.0017	0.0088	0.0086	0.0088	−0.0014	−0.0281	0.0084
56.66	0.9861	1.3860	−0.0308	−0.0019	0.0097	0.0094	0.0096	−0.0011	−0.0313	0.0092
46.89	0.9929	1.3789	−0.0305	−0.0015	0.0099	0.0096	0.0097	−0.0011	−0.0310	0.0094
37.20	0.9972	1.3704	−0.0277	−0.0015	0.0088	0.0086	0.0086	−0.0011	−0.0284	0.0084
27.91	0.9985	1.3612	−0.0221	−0.0014	0.0068	0.0066	0.0066	−0.0007	−0.0230	0.0064
18.73	0.9979	1.3517	−0.0147	−0.0010	0.0045	0.0043	0.0043	−0.0005	−0.0154	0.0042
9.37	0.9970	1.3421	−0.0070	−0.0004	0.0021	0.0020	0.0020	−0.0008	−0.0073	0.0019
0	0.9970	1.3328	0	0	0	0	0	0	0	0

[a] Data apply to the sodium D line and temperature of 25 ± 0.01 °C. [b] Observed density. [c] Observed refractive index. [d] Volume change on mixing calculated from eq 7. [e] Refractive index calculated by using eq 2a–6a*.

Table III. Mixtures of H_2O (1) and PrOEtOH (2)[a]

p_2, wt %	ρ_{12},[b] g/cm^3	n_{12} obsd[c]	ΔV,[d] cm^3	$\Delta n = n_{12}$ obsd $- n_{12}$ calcd[e]						
				eq 2a	eq 2a*	eq 3a*	eq 4a*	eq 5a	eq 6a	eq 5a* and 6a*
100	0.9074	1.4122	0	0	0	0	0.0008	0	0	0
87.65	0.9279	1.4064	−0.0121	−0.0016	0.0027	0.0025	0.0032	−0.0013	−0.0125	0.0024
76.64	0.9434	1.3998	−0.0189	−0.0027	0.0041	0.0039	0.0044	−0.0022	−0.0200	0.0037
65.83	0.9566	1.3928	−0.0228	−0.0029	0.0054	0.0051	0.0055	−0.0024	−0.0242	0.0047
56.29	0.9663	1.3861	−0.0239	−0.0022	0.0063	0.0059	0.0062	−0.0020	−0.0252	0.0057
46.64	0.9755	1.3787	−0.0241	−0.0021	0.0067	0.0063	0.0065	−0.0017	−0.0252	0.0061
37.06	0.9836	1.3706	−0.0230	−0.0020	0.0062	0.0061	0.0062	−0.0017	−0.0243	0.0059
27.58	0.9902	1.3618	−0.0204	−0.0020	0.0055	0.0053	0.0053	−0.0016	−0.0218	0.0051
18.39	0.9941	1.3526	−0.0153	−0.0015	0.0042	0.0039	0.0040	−0.0013	−0.0164	0.0038
9.15	0.9955	1.3424	−0.0076	−0.0009	0.0018	0.0017	0.0017	−0.0009	−0.0084	0.0016
0	0.9970	1.3328	0	0	0	0	0	0	0	0

[a] Data apply to the sodium D line and temperature of 25 ± 0.01 °C. [b] Observed density. [c] Observed refractive index. [d] Volume change on mixing, calculated from eq 7. [e] Refractive index calculated by using eq 2a–6a*.

Table IV. Mixtures of H_2O (1) and i-PrOEtOH (2)[a]

p_2, wt %	ρ_{12},[b] g/cm^3	n_{12} obsd[c]	ΔV,[d] cm^3	$\Delta n = n_{12}$ obsd $- n_{12}$ calcd[e]						
				eq 2a	eq 2a*	eq 3a*	eq 4a*	eq 5a	eq 6a	eq 5a* and 6a*
100	0.9996	1.4081	0	0	0	0	0.0007	0	0	0
87.55	0.9241	1.4060	−0.0160	−0.0014	0.0043	0.0042	0.0047	−0.0008	−0.0155	0.0041
76.36	0.9423	1.3993	−0.0247	−0.0023	0.0066	0.0065	0.0069	−0.0014	−0.0248	0.0063
65.76	0.9570	1.3928	−0.0295	−0.0030	0.0077	0.0076	0.0078	−0.0020	−0.0303	0.0073
55.93	0.9690	1.3867	−0.0318	−0.0027	0.0090	0.0088	0.0090	−0.0017	−0.0325	0.0085
46.04	0.9792	1.3792	−0.0318	−0.0026	0.0092	0.0089	0.0090	−0.0017	−0.0328	0.0087
36.63	0.9872	1.3712	−0.0298	−0.0025	0.0086	0.0084	0.0084	−0.0015	−0.0311	0.0081
27.23	0.9925	1.3624	−0.0252	−0.0019	0.0074	0.0072	0.0072	−0.0013	−0.0261	0.0070
18.14	0.9948	1.3527	−0.0175	−0.0014	0.0051	0.0049	0.0049	−0.0010	−0.0184	0.0048
9.11	0.9955	1.3423	−0.0084	−0.0010	0.0021	0.0020	0.0020	−0.0009	−0.0092	0.0019
0	0.9970	1.3328	0	0	0	0	0	0	0	0

[a] Data apply to the sodium D line and temperature of 25 ± 0.01 °C. [b] Observed density. [c] Observed refractive index. [d] Volume change on mixing, calculated from eq 7. [e] Refractive index calculated by using eq 2a–6a*.

Table V.   Mixtures of H_2O (1) and BuOEtOH (2)[a]

				$\Delta n = n_{12}\text{obsd} - n_{12}\text{calcd}$ [e]						
p_2, wt %	ρ_{12},[b] g/cm³	n_{12} obsd [c]	ΔV,[d] cm³	eq 2a	eq 2a*	eq 3a*	eq 4a*	eq 5a	eq 6a	eq 5a* and 6a*
100	0.8969	1.4176	0	0	0	0	0.0009	0	0	0
87.91	0.0161	1.4106	−0.0098	−0.0015	0.0018	0.0017	0.0025	−0.0013	−0.0104	0.0017
76.59	0.9305	1.4032	−0.0141	−0.0015	0.0034	0.0031	0.0038	−0.0013	−0.0144	0.0030
66.51	0.9421	1.3957	−0.0160	−0.0015	0.0041	0.0038	0.0043	−0.0014	−0.0165	0.0040
56.27	0.9592	1.3875	−0.0161	−0.0012	0.0046	0.0042	0.0046	−0.0011	−0.0165	0.0040
46.76	0.9620	1.3789	−0.0155	−0.0012	0.0044	0.0040	0.0043	−0.0011	−0.0161	0.0038
36.81	0.9710	1.3701	−0.0143	−0.0011	0.0041	0.0037	0.0039	−0.0011	−0.0151	0.0035
27.29	0.9798	1.3616	−0.0129	−0.0007	0.0040	0.0037	0.0038	−0.0007	−0.0134	0.0036
18.01	0.9880	1.3527	−0.0110	−0.0006	0.0034	0.0032	0.0033	−0.0005	−0.0114	0.0029
9.03	0.9944	1.3430	−0.0075	−0.0008	0.0019	0.0018	0.0018	−0.0008	−0.0082	0.0017
0	0.9970	1.3328	0	0	0	0	0	0	0	0

[a] Data apply to the sodium D line and temperature of 25 ± 0.01 °C.   [b] Observed density.   [c] Observed refractive index.   [d] Volume change on mixing, calculated from eq 7.   [e] Refractive index calculated by using eq 2a–6a*.

Table VI.   Mixtures of H_2O (1) and *i*-BuOEtOH (2)[a]

				$\Delta n = n_{12}\text{obsd} - n_{12}\text{calcd}$ [e]						
p_2, wt %	ρ_{12},[b] g/cm³	n_{12} obsd [c]	ΔV,[d] cm³	eq 2a	eq 2a*	eq 3a*	eq 4a*	eq 5a	eq 6a	eq 5a* and 6a*
100	0.8915	1.4158	0	0	0	0	0.0009	0	0	0
87.66	0.9122	1.4100	−0.0108	−0.0009	0.0029	0.0028	0.0036	−0.0005	−0.0104	0.0027
76.79	0.9273	1.4032	−0.0156	−0.0011	0.0044	0.0042	0.0048	−0.0007	−0.0154	0.0040
66.11	0.9400	1.3955	−0.0176	−0.0010	0.0052	0.0049	0.0054	−0.0006	−0.0173	0.0048
56.10	0.9511	1.3874	−0.0182	−0.0010	0.0054	0.0050	0.0054	−0.0008	−0.0181	0.0048
46.38	0.9612	1.3792	−0.0177	−0.0009	0.0053	0.0050	0.0052	−0.0007	−0.0178	0.0047
36.61	0.9710	1.3704	−0.0166	−0.0009	0.0045	0.0045	0.0047	−0.0008	−0.0170	0.0043
27.58	0.9810	1.3622	−0.0154	−0.0008	0.0045	0.0042	0.0043	−0.0007	−0.0159	0.0040
18.01	0.9894	1.3532	−0.0137	−0.0007	0.0039	0.0037	0.0038	−0.0006	−0.0142	0.0035
8.92	0.9956	1.3436	−0.0092	−0.0005	0.0025	0.0023	0.0024	−0.0004	−0.0096	0.0023
0	0.9982	1.3331	0	0	0	0	0	0	0	0

[a] Data apply to the sodium D line and temperature of 20 ± 0.01 °C.   [b] Observed density.   [c] Observed refractive index.   [d] Volume change on mixing, calculated from eq 7.   [e] Refractive index calculated by using eq 2a–6a*.

Table VII.   Mixtures of H_2O (1) and MeOPrOH (2)[a]

				$\Delta n = n_{12}\text{obsd} - n_{12}\text{calcd}$ [e]						
p_2, wt %	ρ_{12},[b] g/cm³	n_{12} obsd [c]	ΔV,[d] cm³	eq 2a	eq 2a*	eq 3a*	eq 4a	eq 5a	eq 6a	eq 5a* and 6a*
100	0.9425	1.4102	0	0	0	0	0.0008	0	0	0
87.94	0.9605	1.4062	−0.0129	−0.0006	0.0043	0.0040	0.0047	−0.0001	−0.0124	0.0041
76.93	0.9734	1.4002	−0.0203	−0.0013	0.0063	0.0060	0.0065	−0.0007	−0.0204	0.0059
67.09	0.9821	1.3936	−0.0237	−0.0018	0.0071	0.0067	0.0072	−0.0010	−0.0243	0.0067
57.04	0.9883	1.3860	−0.0243	−0.0017	0.0074	0.0071	0.0074	−0.0011	−0.0250	0.0069
47.28	0.9924	1.3778	−0.0288	−0.0016	0.0070	0.0066	0.0069	−0.0010	−0.0236	0.0065
37.80	0.9946	1.3687	−0.0195	−0.0018	0.0055	0.0052	0.0053	−0.0014	−0.0208	0.0050
28.32	0.9955	1.3600	−0.0149	−0.0011	0.0045	0.0042	0.0043	−0.0009	−0.0157	0.0041
18.90	0.9957	1.3506	−0.0097	−0.0009	0.0027	0.0025	0.0025	−0.0008	−0.0104	0.0023
9.41	0.9960	1.3410	−0.0046	−0.0010	0.0007	0.0006	0.0006	−0.0010	−0.0054	0.0005
0	0.9970	1.3328	0	0	0	0	0	0	0	0

[a] Data apply to the sodium D line and temperature of 25 ± 0.01 °C.   [b] Observed density.   [c] Observed refractive index.   [d] Volume change on mixing, calculated from eq 7.   [e] Refractive index calculated by using eq 2a–6a*.

Table VIII.   Mixtures of H_2O (1) and EtOPrOH (2)[a]

				$\Delta n = n_{12}\text{obsd} - n_{12}\text{calcd}$ [e]						
p_2, wt %	ρ_{12},[b] g/cm³	n_{12} obsd [c]	ΔV,[d] cm³	eq 2a	eq 2a*	eq 3a*	eq 4a*	eq 5a	eq 6a	eq 5a* and 6a*
100	0.9153	1.4147	0	0	0	0	0.0009	0	0	0
87.71	0.9382	1.4106	−0.0157	−0.0013	0.0044	0.0042	0.0050	−0.0007	−0.0154	0.0042
76.76	0.9541	1.4049	−0.0236	−0.0017	0.0070	0.0067	0.0073	−0.0009	−0.0235	0.0066
66.15	0.9666	1.3971	−0.0277	−0.0026	0.0076	0.0072	0.0077	−0.0018	−0.0286	0.0071
55.94	0.9759	1.3880	−0.0284	−0.0036	0.0069	0.0065	0.0069	−0.0029	−0.0306	0.0063
46.51	0.9828	1.3806	−0.0271	−0.0025	0.0075	0.0071	0.0073	−0.0020	−0.0286	0.0069
37.08	0.9880	1.3716	−0.0241	−0.0024	0.0066	0.0062	0.0064	−0.0019	−0.0257	0.0060
27.62	0.9914	1.3618	−0.0191	−0.0021	0.0050	0.0047	0.0048	−0.0018	−0.0207	0.0045
18.52	0.9933	1.3522	−0.0128	−0.0014	0.0033	0.0031	0.0031	−0.0013	−0.0141	0.0029
9.14	0.9948	1.3412	−0.0060	−0.0017	0.0005	0.0003	0.0004	−0.0017	−0.0076	0.0003
0	0.9970	1.3328	0	0	0	0	0	0	0	0

[a] Data apply to the sodium D line and temperature of 25 ± 0.01 °C.   [b] Observed density.   [c] Observed refractive index.   [d] Volume change on mixing, calculated from eq 7.   [e] Refractive index calculated by using eq 2a–6a*.

where

$$A =$$

$$\left[\left(\frac{n_1{}^2 - 1}{n_1{}^2 + 2} \right) \frac{1}{\rho_1} - \left(\frac{n_1{}^2 - 1}{n_1{}^2 + 2} \right) \frac{p_2}{\rho_1} \left(\frac{n_2{}^2 - 1}{n_2{}^2 + 2} \right) \frac{p_2}{\rho_2} \right] \rho_{12}$$

$$n_{12} = \left[\frac{2B(p_2\rho_{12}/\rho_2) + n_1{}^2}{1 - B(p_2\rho_{12}/\rho_2)} \right]^{1/2} \quad (2a)^*$$

where

$$B = \frac{n_2{}^2 - n_1{}^2}{n_2{}^2 + 2}$$

$$n_{12} = n_1 \left(\frac{1 + 2C}{1 - C} \right)^{1/2} \quad (3a)^*$$

where

$$C = \frac{p_2\rho_{12}}{\rho_2} \left(\frac{m_1{}^2 - 1}{m_2{}^2 + 2} \right)$$

$$n_{12} = \frac{3}{2} \frac{p_2\rho_{12}}{\rho_2} \frac{m^2 - 1}{m^2 + 2} n_1 + n_1 \quad (4a)^*$$

$$n_{12} = \rho_{12} \left[\frac{n_1 - 1}{\rho_1} - (n_1 - 1)\frac{p_2}{\rho_1} + (n_2 - 1)\frac{p_2}{\rho_2} \right] + 1 \quad (5a)$$

$$n_{12} = \rho_{12} \left[\frac{n_1}{\rho_1} + p_2 \left(\frac{n_2}{\rho_1} - \frac{n_1}{\rho_2} \right) \right] \quad (6a)$$

$$n_{12} = (n_2 - n_1)(p_2\rho_{12}/\rho_2) + n_1 \quad (5a)^* \text{ and } (6a)^*$$

Asterisks indicate that the respective equation is formulated for the case of volume additivity. The results are tabulated in Tables I–VIII. In these tables, ΔV is the change in volume on mixing of the pure components defined as

$$\Delta V = \frac{1}{\rho_{12}{}^{obsd}} - \frac{1}{\rho_{12}{}^{calcd}} \quad (7)$$

$$\frac{1}{\rho_{12}{}^{calcd}} = \frac{1}{\rho_1} + p_2 \left(\frac{1}{\rho_2} - \frac{1}{\rho_1} \right) \quad (8)$$

where $\rho_{12}{}^{obsd}$ and $\rho_{12}{}^{calcd}$ are the densities of solution observed and calculated according to eq 8, respectively. Δn is the difference in refractive index of solution defined as

$$\Delta n = n_{12}{}^{obsd} - n_{12}{}^{calcd} \quad (9)$$

where $n_{12}{}^{obsd}$ and $n_{12}{}^{calcd}$ are the refractive indices of solution observed and calculated by using the refractive index mixture rules, respectively.

The Lorentz–Lorenz equation (2a) and the Gladstone–Dale equation (5a) are seen to perform considerably well and far better than all others. The Arago–Biot equation (6a) is very unsatisfactory. It is noticed in common for all the systems investigated that eq 2a*, 3a*, 4a*, 5a*, and 6a* give almost the same values to Δn for the system under discussion, which are about from 2 to 5 times larger than the values calculated from eq 2a and 5a depending upon the system.

It is found in all the systems that there are good linear relationships given by

$$\Delta n(p_2) = k_1 \Delta V(p_2) \quad (10)$$

and

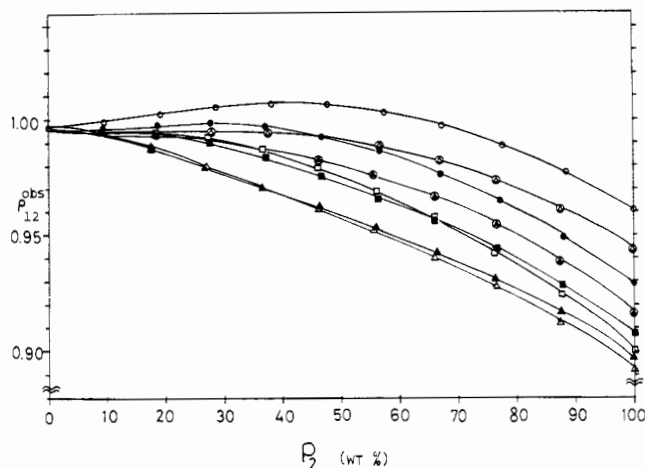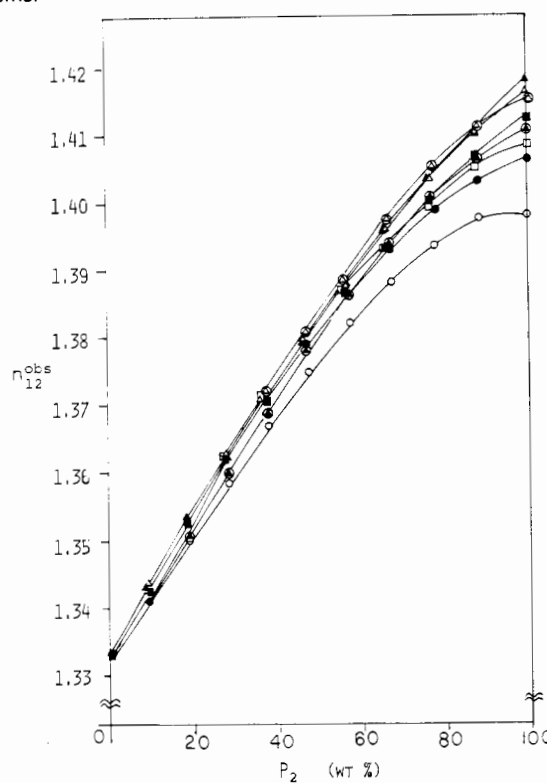$$\Delta n^*(p_2) = k_2 \Delta V(p_2) \quad (11)$$

Figure 1. Plots of densities against weight fraction of alkoxy alcohols; p_2 is wt % of alcohol: (O) MeOEtOH–H$_2$O, (●) EtOEtOH–H$_2$O, (■) PrOEtOH–H$_2$O, (□) i-PrOEtOH–H$_2$O, (▲) BuOEtOH–H$_2$O, (△) i-BuOEtOH–H$_2$O, (circled △) MeOPrOH–H$_2$O, (circled ▲) EtOPrOH–H$_2$O systems.

Figure 2. Plots of refractive indices against weight fraction of alkoxy alcohols; p_2 is wt % of alcohol: (O) MeOEtOH–H$_2$O, (●) EtOEtOH–H$_2$O, (■) PrOEtOH–H$_2$O, (□) i-PrOEtOH–H$_2$O, (▲) BuOEtOH–H$_2$O, (△) i-BuOEtOH–H$_2$O, (circled ▲) MeOPrOH–H$_2$O, (circled △) EtOPrOH–H$_2$O systems.

Table IX.   The Values of k_1 and k_2

system	k_1	k_2
MeOEtOH–H$_2$O	0.071	0.30
EtOEtOH–H$_2$O	0.057	0.31
PrOEtOH–H$_2$O	0.106	0.26
i-PrOEtOH–H$_2$O	0.087	0.28
BuOEtOH–H$_2$O	0.086	0.27
i-BuOEtOH–H$_2$O	0.058	0.29
MeOPrOH–H$_2$O	0.078	0.29
EtOPrOH–H$_2$O	0.104	0.26

respectively. Here, the asterisk indicates that the values are obtained from the equation formulated on the basis of volume additivity. The values of k_1 and k_2 obtained from the least-squares method are tabulated in Table IX. It is noted from Table IX that the values of k_2 are almost equal in all the aqueous

mixtures investigated, whereas k_1 takes different values depending upon the system under discussion. These results clearly indicate the presence of a correlation between ΔV and Δn. This is not unexpected because ΔV, which is the deviation from volume additivity, i.e., ideality, can be considered as a measure of interaction between the components and Δn, which is closely related to the change in molecular polarizabilities on mixing of the components,[4] is also a barometer of interaction between the components.

The following general tendencies concerning ΔV and k_1 are recognized from those tables: (1) The values of k_1 are small in EtOEtOH–H_2O and *i*-BuOEtOH–H_2O systems but large in PrOEtOH–H_2O and EtOPrOH–H_2O systems. (2) The values of ΔV are small in BuOEtOH–H_2O and *i*-BuOEtOH–H_2O systems but large in EtOEtOH–H_2O and *i*-PrOEtOH–H_2O systems. (3) The methoxy group induces larger changes in ΔV than the ethoxy group. (4) Isoalkoxyethanol–water systems have larger values of ΔV than *n*-alkoxyethanol–water systems. On the contrary, the former systems have smaller values of k_1 than the latter systems. (5) It is reported that the ability of forming an intramolecular hydrogen bond is larger in MeOPrOH than in MeOEtOH and in EtOPrOH than in EtOEtOH.[11] The values of ΔV

are smaller in the MeOPrOH–H_2O system than in the MeOEtOH–H_2O system and smaller in the EtOPrOH–H_2O system than in the EtOEtOH–H_2O system. On the other hand, the value of k_1 is larger in the MeOPrOH–H_2O system than in the MeOEtOH–H_2O system and larger in the EtOPrOH–H_2O system than in the EtOEtOH–H_2O system. The intramolecular hydrogen bonding ability of molecules seems to have great influence on not only ΔV but also Δn.

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Solubility of Cuprous Chloride in Aqueous Hydrochloric Acid Solutions[†]

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The solubilities of cuprous chloride in water and hydrochloric acid solutions were determined at different temperatures. Effects of temperature and hydrochloric acid concentration on the solubility were correlated by the equation ln $S = a + b/T + c$ ln $(1 + dX)$ where S, X, and T are respectively solubility, concentration of hydrochloric acid, and temperature in K, and a, b, c, and d are constants.

Table I. Solubility Data for the $CuCl$-HCl-H_2O System

concn of HCl, g-mol/L	solubility of CuCl, $S \times 10^2$, g-mol/L			
	20 °C	29 °C	40 °C	50 °C
0.0	0.295	0.380	0.519	0.668
0.129	0.944	1.175	1.603	1.927
0.158	1.122	1.380	1.884	2.238
0.266	1.698	2.113	2.985	3.467
0.398	2.398	2.985	4.121	4.897
0.603	3.388	4.168	5.888	6.839

Introduction

Solubilities of sparingly soluble solids in liquids are often required in studies on mass transfer in solid–liquid systems. Such data are also important in systems where gas absorption in slurries is followed by its reaction with a simultaneously dissolving solid. The present studies on the solubility of CuCl in aqueous HCl solutions were undertaken in view of their importance in a number of reactions, such as in the reactions of acetylene (*1*) and of oxygen (*3*) with cuprous chloride.

The solubility of CuCl in water was studied in the temperature range 20–50 °C. The effect of HCl concentration at various temperatures was also investigated.

Experimental Section

The solubility experiments were carried out in a magnetically stirred vessel provided with a jacket for circulating water at

constant temperature. A constant temperature (±0.1 °C) was maintained using a thermostatic bath.

Freshly prepared cuprous chloride stored in a vacuum desiccator was used throughout the work. High-purity nitrogen gas, passed through a pyrogallol solution, was used for flushing purposes. Reagents used for analysis were of AR grade.

In a typical run, the jacketed vessel was thoroughly flushed with nitrogen, and 100 mL of degassed, distilled water was charged with an excess of cuprous chloride. Nitrogen gas was constantly kept bubbling through the slurry, which was magnetically stirred using a Teflon-coated needle. A constant temperature was maintained in the vessel by circulating water through the outer jacket, from a thermostat set at the required temperature.

Samples were withdrawn at intervals of 5–10 min for analysis, and this was continued until saturation was indicated by constancy of two to three consecutive readings. Dissolved cuprous chloride in the samples was analyzed by a method described by Vogel (*2*).

In all the experiments, precautions were taken to maintain an oxygen-free atmosphere throughout, since cuprous chloride