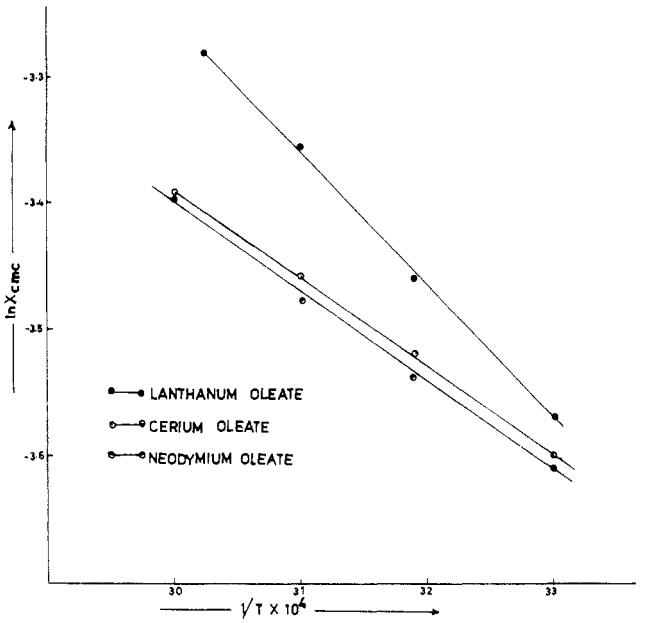

Figure 5. ln X_{cmc} vs $1/T$ plots for lanthanide metal oleates.

of the phase separation model and conductivity measurements. The results showed that the micellization process is predominant over the dissociation process and lanthanide soaps behaved as a weak electrolyte in benzene–methanol mixture.

Registry No. Lanthanum oleate, 94232-46-9; cerium oleate, 94232-60-7; neodymium oleate, 90568-80-2; benzene, 71-43-2; methanol, 67-56-1.

Literature Cited

(1) Mehrotra, R. C. *Wiss. Z. Friedrich-Schiller Univ. Jena Math. Naturwiss. Reihe.* **1965**, *14*, 171.
(2) Skellon, J. H.; Andrews, K. E. *J. Appl. Chem. London*, **1955**, *5*, 245.
(3) Ryan, L. W.; Piechnar, W. W. *Ind. Eng. Chem.* **1934**, *26*, 909.
(4) Chatfield, H. W. *Paint Manuf.* **1936**, *6*, 112.
(5) Skrylev, L. D.; Sazonna, V. F.; Kornelli, M. E.; Shumitina, N. A. *Khim. Khim. Tekhnol.* **1978**, *21*, 491.
(6) Skellon, J. H.; Spence, J. W. *J. Appl. Chem. London*, **1953**, *3*, 10.
(7) Titanium Pigment Co. Inc. Brit. **1933**, *17*, 395-406.
(8) Misra, S. N.; Misra, T. N.; Mehrotra, R. C. *J. Inorg. Nucl. Chem.* **1963**, *25*, 195-201.
(9) Skellon, J. H.; Spence, J. W. *J. Soc. Chem. Ind. London* **1948**, *67*, 365.
(10) Morwedel, G.; *Farbe + Lack* **1954**, *60*, 530, **1956**, *62*, 92.
(11) Main, F.; Mills, D.; White, D. W. U.S. Patent 3 320 172, 1967.
(12) Bhandari, A. M.; Dubey, S.; Kapoor, R. N. *J. Am. Oil Chemist's Soc.* **1970**, *4*, 47.
(13) Solanki, A. K.; Bhandari, A. M. *Tenside Detergents*, **1961**, *18*, 34.
(14) Varma, R. P.; Jindal, R. *Tenside Detergents*, **1983**, *20*, 193.
(15) Mehrotra, K. N.; Gahlaut, A. S.; Sharma, Merra. *J. Am. Oil Chemists Soc.* **1986**, *63*, 1571.
(16) Mehrotra, K. N.; Gahlaut, A. S.; Sharma, Meera, *J. Colloid Interface Sci.* **1987**, *1(120)*, 110.
(17) Barry, B. W.; Russel, G. F. J. *J. Colloid Interface Sci.* **1972**, *40*, 174.
(18) Robins, D. C.; Thomas, I. L. *J. Colloid Interface Sci.* **1968**, *26*, 407.

Received for review November, 17, 1987. Accepted May 31, 1988. Grateful thanks are extended to UGC, New Delhi, for financial assistance to S.K.U.

Liquid–Liquid Equilibrium Data for the Ternary Systems Water–Ethyl Alcohol–Organic Acid (Hexanoic, Heptanoic, Octanoic, and Nonanoic Acid) and Water–Ethyl Alcohol–Phthalic Acid Dialkyl Ester (Diethyl, Dibutyl, and Dioctyl Ester)

Isidoro G. García,* Arturo Ch. Pérez, and Francisca C. Calero

Departamento de Ingeniería Química, Facultad de Ciencias, C/San Alberto Magno s/n, 14004-Córdoba, Spain

The liquid–liquid equilibrium data for the ternary systems water–ethyl alcohol–organic acid (hexanoic, heptanoic, octanoic, and nonanoic acid) and water–ethyl alcohol–phthalic acid dialkyl ester (diethyl, dibutyl, and dioctyl ester) have been determined at 298 K. The data were compared with those obtained from the UNIFAC method. Finally, densities of the conjugated phases have been determined.

Introduction

The use of ethanol obtained from fermented waste rich in carbohydrates is already well-known (*1*).

Liquid–liquid extraction is a technique known to separate the ethanol from water mixtures; it is an alternative to distillation. Liquid–liquid extraction allows us to obtain high-standard ethanol. This also lowers the energy cost of the process in comparison to distillation (*1*). We are trying to find an adequate solvent for the extraction of the ethanol from the water mixtures; for this reason, in this research we have determined the equilibrium data of the aforesaid systems which have not been found in the literature.

Table I. Experimental and Literature Values for the Refractive Indexes at 293 K, n^{293}_D, of the Chemicals Used

chemical	exptl	ref *2*	ref *3*
ethyl alcohol	1.3610	1.3610	1.3611
hexanoic acid	1.4160	1.4163	1.4163
heptanoic acid	1.4218	1.4216	1.4170
octanoic acid	1.4278	1.4280	1.4285
nonanoic acid	1.4328	1.4330	1.4343
phthalic acid diethyl ester	1.5003	1.5049[a]	1.5000
phthalic acid dibutyl ester	1.4910	1.4900	1.4911
phthalic acid dioctyl ester	1.4864		1.4867

[a] Measured at 287 K.

Experimental Section

Chemicals. Twice distilled water, ethyl alcohol (Panreac 99.5%), hexanoic acid (Fluka 99.5%), heptanoic acid (Fluka 99%), octanoic acid (Fluka 99.6%), nonanoic acid (Fluka 97%), phthalic acid diethyl ester (Merck 99%), phthalic acid

0021-9568/88/1733-0468$01.50/0

Table II. Binodal-Curve Data for the System Water (1)-Ethanol (2)-Hexanoic Acid (3) at 298 K

x(1)	x(2)	x(3)	n_D[a]	x(1)	x(2)	x(3)	n_D[a]
0.999	0.000	0.001	1.3342	0.593	0.233	0.174	1.3864
0.933	0.065	0.002	1.3446	0.563	0.227	0.210	1.3898
0.902	0.095	0.003	1.3486	0.529	0.214	0.257	1.3941
0.893	0.103	0.004	1.3499	0.491	0.194	0.315	1.3980
0.875	0.117	0.008	1.3527	0.477	0.182	0.341	1.4003
0.842	0.138	0.021	1.3578	0.462	0.160	0.379	1.4021
0.805	0.158	0.037	1.3635	0.435	0.140	0.425	1.4043
0.775	0.175	0.050	1.3670	0.405	0.115	0.480	1.4068
0.743	0.190	0.068	1.3714	0.391	0.085	0.524	1.4088
0.681	0.216	0.103	1.3775	0.360	0.075	0.565	1.4098
0.652	0.223	0.125	1.3810	0.318	0.041	0.641	1.4120
0.624	0.230	0.146	1.3837	0.280	0.011	0.709	1.4133

[a] Refractive index.

Table III. Binodal-Curve Data for the System Water (1)-Ethanol (2)-Heptanoic Acid (3) at 298 K

x(1)	x(2)	x(3)	n_D	x(1)	x(2)	x(3)	n_D
0.980	0.020	0.000	1.3363	0.553	0.279	0.168	1.3900
0.958	0.042	0.000	1.3396	0.512	0.276	0.212	1.3945
0.952	0.048	0.000	1.3410	0.481	0.265	0.255	1.3984
0.916	0.083	0.001	1.3461	0.454	0.239	0.308	1.4025
0.851	0.143	0.006	1.3548	0.422	0.215	0.363	1.4059
0.823	0.163	0.014	1.3589	0.398	0.185	0.418	1.4093
0.797	0.180	0.024	1.3626	0.373	0.151	0.475	1.4116
0.768	0.197	0.035	1.3665	0.340	0.125	0.535	1.4140
0.722	0.222	0.056	1.3722	0.307	0.087	0.606	1.4163
0.685	0.241	0.074	1.3760	0.273	0.065	0.662	1.4178
0.633	0.264	0.103	1.3814	0.235	0.037	0.729	1.4194
0.595	0.276	0.129	1.3852	0.210	0.000	0.790	1.4205

dibutyl ester (Merck 99%), and phthalic acid dioctyl ester (Carlo Erba 99%) were used.

The solvents were vacuum distilled before their use. The first and last portions of the distillate were discarded. The purity of each chemical was verified by the refraction index measured in an ATAGO Model 3 refractometer. The values that have been found are shown, in comparison to the literature values (*2*, *3*), in Table I.

Procedures and Apparatus. The experimental measurements corresponding to the binodal curve have been determined in a closed glass thermostated receptacle with a capacity of up to 250 cm^3. On top it has four ports, three of them for the titration and the fourth for sampling.

Volumes of up to 125 cm^3 were well mixed by means of a magnetic stirrer.

The method used consisted of the addition of the adequate component or components to a mixture of known composition until a slight turbidity became visible, which did not disappear when agitated (*4*).

The tie lines are determined by analysis of the phases in which one mixture, of known composition situated inside the two-phase region, is separated. The liquid mixture was agitated for several hours before letting the two phases separate. This was carried out in a thermostated decanter with a 50-cm^3 capacity. The analysis of the conjugated phase was carried out by the measurement of its refractive indexes in the ATAGO refractometer (previously we had obtained curves using the refraction index vs composition for the points of the binodal curve).

Finally, the densities of the conjugated phases were determined, with a precision of ±0.002 g/cm^3, by a bulk densimeter with a 50-cm^3 capacity.

Results

The compositions of the binodal curve points and the refractive indexes, determined with a precision of ±0.0005 and ±0.0002 units, respectively, are shown in Tables II–VIII. The compositions are expressed in molar fractions.

Table IV. Binodal-Curve Data for the System Water (1)-Ethanol (2)-Octanoic Acid (3) at 298 K

x(1)	x(2)	x(3)	n_D	x(1)	x(2)	x(3)	n_D
0.980	0.020	0.000	1.3363	0.550	0.311	0.140	1.3902
0.958	0.042	0.000	1.3396	0.515	0.310	0.175	1.3945
0.935	0.065	0.000	1.3429	0.497	0.306	0.197	1.3970
0.911	0.089	0.000	1.3463	0.472	0.302	0.225	1.3998
0.894	0.106	0.000	1.3490	0.440	0.287	0.273	1.4036
0.866	0.133	0.001	1.3521	0.434	0.275	0.292	1.4055
0.836	0.159	0.005	1.3557	0.400	0.250	0.350	1.4092
0.801	0.186	0.014	1.3607	0.382	0.224	0.393	1.4120
0.765	0.209	0.026	1.3660	0.345	0.195	0.460	1.4150
0.728	0.232	0.040	1.3707	0.310	0.155	0.535	1.4183
0.693	0.252	0.055	1.3749	0.271	0.114	0.616	1.4211
0.643	0.279	0.079	1.3798	0.225	0.054	0.721	1.4237
0.590	0.298	0.112	1.3859	0.168	0.000	0.832	1.4261

Table V. Binodal-Curve Data for the System Water (1)-Ethanol (2)-Nonanoic Acid (3) at 298 K

x(1)	x(2)	x(3)	n_D	x(1)	x(2)	x(3)	n_D
0.980	0.020	0.000	1.3363	0.551	0.328	0.121	1.3904
0.958	0.042	0.000	1.3396	0.511	0.334	0.155	1.3952
0.935	0.065	0.000	1.3429	0.496	0.329	0.175	1.3977
0.911	0.089	0.000	1.3462	0.476	0.325	0.199	1.4005
0.885	0.115	0.000	1.3498	0.445	0.315	0.240	1.4048
0.858	0.141	0.000	1.3531	0.418	0.305	0.278	1.4077
0.848	0.151	0.001	1.3539	0.387	0.279	0.333	1.4118
0.803	0.189	0.008	1.3593	0.376	0.254	0.370	1.4144
0.786	0.201	0.013	1.3622	0.330	0.210	0.460	1.4193
0.756	0.221	0.022	1.3664	0.282	0.159	0.559	1.4232
0.701	0.258	0.041	1.3734	0.257	0.128	0.615	1.4250
0.690	0.264	0.046	1.3750	0.232	0.110	0.658	1.4260
0.655	0.284	0.061	1.3788	0.196	0.059	0.745	1.4283
0.598	0.309	0.093	1.3858	0.137	0.000	0.863	1.4306

Table VI. Binodal-Curve Data for the System Water (1)-Ethanol (2)-Phthalic Acid Diethyl Ester (3) at 298 K

x(1)	x(2)	x(3)	n_D	x(1)	x(2)	x(3)	n_D
0.980	0.020	0.000	1.3363	0.457	0.358	0.185	1.4397
0.958	0.042	0.000	1.3396	0.430	0.361	0.209	1.4444
0.935	0.065	0.000	1.3429	0.389	0.356	0.255	1.4523
0.929	0.070	0.000	1.3442	0.344	0.346	0.310	1.4610
0.891	0.108	0.001	1.3494	0.315	0.333	0.352	1.4646
0.875	0.124	0.001	1.3518	0.290	0.315	0.395	1.4687
0.841	0.157	0.002	1.3559	0.265	0.290	0.445	1.4733
0.814	0.182	0.004	1.3596	0.250	0.267	0.483	1.4766
0.779	0.213	0.007	1.3648	0.220	0.225	0.555	1.4813
0.743	0.244	0.013	1.3711	0.202	0.193	0.605	1.4847
0.693	0.279	0.028	1.3828	0.175	0.137	0.687	1.4892
0.646	0.305	0.048	1.3955	0.150	0.105	0.745	1.4917
0.611	0.320	0.069	1.4056	0.125	0.065	0.810	1.4947
0.567	0.338	0.095	1.4159	0.108	0.037	0.855	1.4970
0.530	0.347	0.124	1.4252	0.099	0.000	0.901	1.4990
0.491	0.355	0.154	1.4326				

Table VII. Binodal-Curve Data for the System Water (1)-Ethanol (2)-Phthalic Acid Dibutyl Ester (3) at 298 K

x(1)	x(2)	x(3)	n_D	x(1)	x(2)	x(3)	n_D
0.980	0.020	0.000	1.3363	0.436	0.493	0.071	1.4061
0.958	0.042	0.000	1.3396	0.386	0.503	0.111	1.4206
0.935	0.065	0.000	1.3429	0.356	0.499	0.145	1.4291
0.911	0.089	0.000	1.3463	0.327	0.493	0.180	1.4373
0.885	0.115	0.000	1.3498	0.300	0.487	0.213	1.4436
0.832	0.168	0.000	1.3550	0.264	0.466	0.270	1.4520
0.792	0.208	0.000	1.3577	0.224	0.446	0.330	1.4588
0.779	0.221	0.001	1.3585	0.229	0.419	0.352	1.4617
0.758	0.241	0.001	1.3597	0.197	0.398	0.405	1.4670
0.719	0.279	0.002	1.3620	0.176	0.363	0.461	1.4718
0.673	0.324	0.004	1.3651	0.161	0.315	0.525	1.4761
0.611	0.380	0.009	1.3706	0.130	0.260	0.610	1.4800
0.565	0.419	0.017	1.3770	0.105	0.180	0.715	1.4840
0.518	0.454	0.028	1.3850	0.081	0.131	0.788	1.4862
0.473	0.479	0.049	1.3966	0.097	0.013	0.890	1.4905

If we compare these results with those estimated by the UNIFAC method (*5*, *6*) we observe, in Figures 1 and 2, how

Table VIII. Binodal-Curve Data for the System Water (1)-Ethanol (2)-Phthalic Acid Dioctyl Ester (3) at 298 K

x(1)	x(2)	x(3)	n_D	x(1)	x(2)	x(3)	n_D
0.980	0.020	0.000	1.3363	0.262	0.696	0.042	1.3960
0.958	0.042	0.000	1.3396	0.252	0.689	0.059	1.4049
0.935	0.065	0.000	1.3429	0.215	0.701	0.083	1.4142
0.911	0.089	0.000	1.3463	0.217	0.689	0.094	1.4192
0.885	0.115	0.000	1.3498	0.199	0.662	0.139	1.4317
0.719	0.280	0.000	1.3602	0.180	0.619	0.201	1.4434
0.667	0.333	0.000	1.3622	0.145	0.585	0.270	1.4538
0.621	0.378	0.001	1.3629	0.135	0.539	0.326	1.4596
0.607	0.393	0.001	1.3632	0.110	0.429	0.461	1.4695
0.569	0.430	0.001	1.3645	0.095	0.387	0.518	1.4720
0.527	0.471	0.002	1.3655	0.074	0.306	0.620	1.4763
0.487	0.519	0.003	1.3678	0.071	0.237	0.692	1.4793
0.418	0.575	0.007	1.3706	0.072	0.155	0.773	1.4818
0.355	0.632	0.013	1.3762	0.082	0.113	0.805	1.4828
0.314	0.665	0.021	1.3824	0.120	0.015	0.865	1.4855
0.289	0.682	0.029	1.3882				

the method predicts the equilibrium correctly from the qualitative point of view but not from the quantitative point of view. There are always some differences that increase as the molecule increases in size; this is so in the case of organic acids. It is contrary to the case of phthalic acid dialkyl esters.

The composition of the conjugated phases, calculated with a precision of ±1%, as well as their corresponding values in their refractive indexes and their densities appear in Tables IX–XV. The densities can be estimated by the following expression

$$\rho_m = \sum^{I} M_I X_I / \sum^{I} \frac{M_I X_i}{\rho_I}$$

where ρ_m is the density of the mixture, M_I is the molecular weight of the component i, ρ_I is the density of the component i and X_I is the mole fraction of the component i.

Table IX. Conjugated Phases Data for the System Water (1)-Ethanol (2)-Hexanoic Acid (3) at 298 K

extract phase					raffinate phase				
x(1)	x(2)	x(3)	n_D	ρ	x(1)	x(2)	x(3)	n_D	ρ
0.394	0.091	0.515	1.4085	0.927	0.979	0.020	0.002	1.3375	0.988
0.432	0.145	0.423	1.4042	0.923	0.958	0.040	0.002	1.3407	0.981
0.494	0.197	0.309	1.3974	0.918	0.938	0.060	0.002	1.3436	0.975
0.550	0.221	0.229	1.3916	0.916	0.920	0.077	0.002	1.3463	0.970
0.610	0.231	0.159	1.3849	0.915	0.897	0.099	0.004	1.3495	0.963

[a] n_D is refractive index and ρ is density.

Table X. Conjugated Phases Data for the System Water (1)-Ethanol (2)-Heptanoic Acid (3) at 298 K

extract phase					raffinate phase				
x(1)	x(2)	x(3)	n_D	ρ	x(1)	x(2)	x(3)	n_D	ρ
0.229	0.099	0.602	1.4160	0.916	0.972	0.028	0.000	1.3376	0.985
0.377	0.161	0.462	1.4112	0.913	0.955	0.045	0.000	1.3404	0.979
0.428	0.220	0.352	1.4054	0.908	0.932	0.067	0.001	1.3438	0.972
0.472	0.254	0.273	1.4000	0.906	0.912	0.087	0.001	1.3466	0.966
0.533	0.273	0.194	1.3929	0.903	0.890	0.108	0.002	1.3494	0.959
0.592	0.276	0.133	1.3857	0.903	0.868	0.128	0.004	1.3524	0.952

Table XI. Conjugated Phases Data for the System Water (1)-Ethanol (2)-Octanoic Acid (3) at 298 K

extract phase					raffinate phase				
x(1)	x(2)	x(3)	n_D	ρ	x(1)	x(2)	x(3)	n_D	ρ
0.268	0.088	0.644	1.4219	0.905	0.978	0.022	0.000	1.3365	0.987
0.312	0.159	0.529	1.4179	0.903	0.954	0.046	0.000	1.3404	0.978
0.382	0.225	0.393	1.4121	0.900	0.929	0.071	0.000	1.3438	0.971
0.418	0.270	0.312	1.4066	0.896	0.911	0.089	0.000	1.3466	0.965
0.471	0.302	0.228	1.4000	0.893	0.889	0.110	0.000	1.3494	0.959
0.530	0.315	0.155	1.3920	0.892	0.866	0.133	0.001	1.3522	0.951

Table XII. Conjugated Phases Data for the System Water (1)-Ethanol (2)-Nonanoic Acid (3) at 298 K

extract phase					raffinate phase				
x(1)	x(2)	x(3)	n_D	ρ	x(1)	x(2)	x(3)	n_D	ρ
0.223	0.087	0.690	1.4269	0.899	0.976	0.024	0.000	1.3368	0.986
0.298	0.164	0.538	1.4226	0.897	0.952	0.048	0.000	1.3404	0.977
0.347	0.235	0.418	1.4170	0.894	0.928	0.072	0.000	1.3439	0.969
0.403	0.280	0.318	1.4109	0.890	0.906	0.094	0.000	1.3471	0.963
0.444	0.312	0.244	1.4048	0.888	0.885	0.115	0.000	1.3495	0.958
0.500	0.332	0.168	1.3969	0.885	0.858	0.141	0.000	1.3524	0.949

Table XIII. Conjugated Phases Data for the System Water (1)-Ethanol (2)-Phthalic Acid Diethyl Ester (3) at 298 K

extract phase					raffinate phase				
x(1)	x(2)	x(3)	n_D	ρ	x(1)	x(2)	x(3)	n_D	ρ
0.089	0.022	0.889	1.4978	1.111	0.975	0.025	0.000	1.3370	0.987
0.116	0.058	0.827	1.4954	1.107	0.949	0.051	0.000	1.3412	0.978
0.138	0.100	0.762	1.4923	1.101	0.919	0.081	0.000	1.3456	0.969
0.182	0.166	0.651	1.4870	1.091	0.887	0.113	0.001	1.3500	0.960
0.232	0.229	0.539	1.4806	1.077	0.854	0.144	0.002	1.3543	0.953
0.293	0.287	0.420	1.4719	1.062	0.814	0.182	0.004	1.3595	0.944
0.346	0.341	0.313	1.4603	1.040	0.772	0.220	0.008	1.3664	0.938

Table XIV. Conjugated Phases Data for the System Water (1)-Ethanol (2)-Phthalic Acid Dibutyl Ester (3) at 298 K

extract phase					raffinate phase				
$x(1)$	$x(2)$	$x(3)$	n_D	ρ	$x(1)$	$x(2)$	$x(3)$	n_D	ρ
0.101	0.040	0.859	1.4899	1.041	0.979	0.021	0.000	1.3365	0.988
0.080	0.073	0.847	1.4884	1.037	0.940	0.060	0.000	1.3423	0.976
0.093	0.133	0.774	1.4860	1.032	0.899	0.101	0.000	1.3480	0.964
0.113	0.198	0.689	1.4830	1.027	0.855	0.145	0.000	1.3529	0.950
0.135	0.270	0.595	1.4792	1.022	0.806	0.194	0.000	1.3569	0.936
0.167	0.330	0.503	1.4746	1.013	0.741	0.258	0.001	1.3607	0.921
0.193	0.384	0.423	1.4684	1.003	0.670	0.327	0.004	1.3654	0.904

Table XV. Conjugated Phases Data for the System Water (1)-Ethanol (2)-Phthalic Acid Dioctyl Ester (3) at 298 K

extract phase					raffinate phase				
$x(1)$	$x(2)$	$x(3)$	n_D	ρ	$x(1)$	$x(2)$	$x(3)$	n_D	ρ
0.119	0.043	0.837	1.4844	0.979	0.969	0.031	0.000	1.3383	0.983
0.091	0.089	0.821	1.4836	0.978	0.931	0.069	0.000	1.3438	0.972
0.096	0.119	0.785	1.4824	0.976	0.892	0.108	0.000	1.3491	0.958
0.068	0.173	0.760	1.4810	0.976	0.849	0.151	0.000	1.3536	0.943
0.065	0.210	0.274	1.4801	0.974	0.785	0.215	0.000	1.3574	0.926
0.069	0.255	0.675	1.4782	0.971	0.726	0.274	0.000	1.3601	0.912
0.072	0.308	0.621	1.4763	0.963	0.667	0.332	0.000	1.3623	0.888
0.067	0.358	0.575	1.4739	0.960	0.558	0.441	0.001	1.3648	0.869
0.099	0.449	0.452	1.4685	0.951	0.458	0.538	0.004	1.3690	0.853

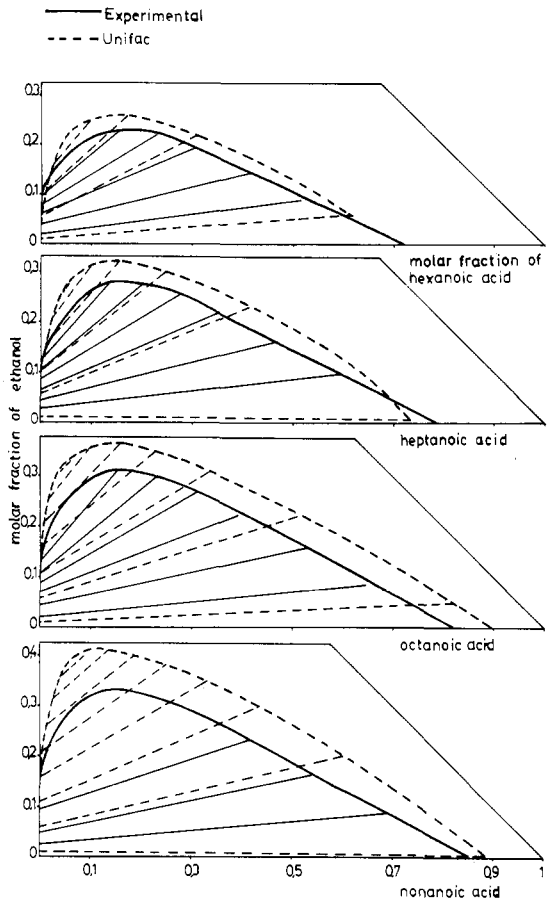

Figure 1. Experimental and UNIFAC calculated liquid–liquid equilibrium for the systems water–ethanol–organic acid (hexanoic, heptanoic, octanoic, and nonanoic acid) at 298 K.

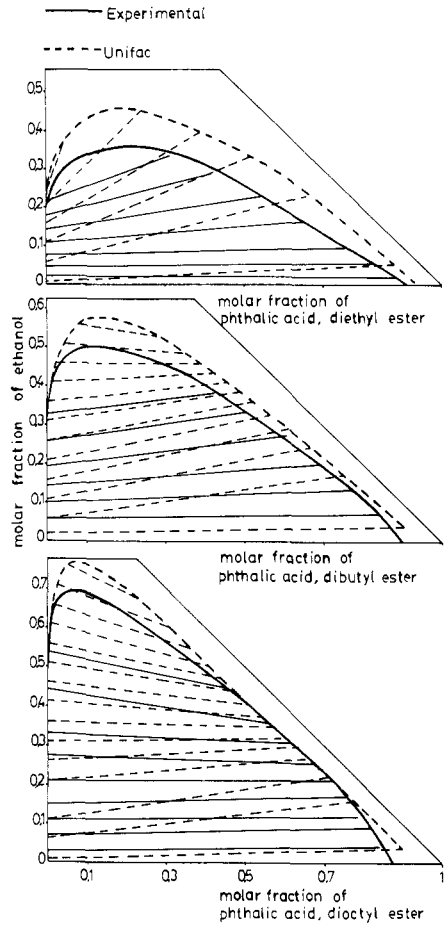

Figure 2. Experimental and UNIFAC calculated liquid–liquid equilibrium for the systems water–ethanol–phthalic acid dialkyl ester (diethyl, dibutyl, and dioctyl ester) at 298 K.

The above expression is obtained from the hypothesis that these mixtures follow the law of additivities of the molar volumes in the pure components; that is

$$V_m = \sum^{I} V_i X_i$$

where V_m is the molar volume of mixture and V_i is the molar volume of the component i.

In this way the densities of the conjugated phases of the organic acids are predicted with a maximum error of 1.48% for the extract phase and 2.43% for the raffinate phase; for the phthalic acid dialkyl esters such an error is 0.89% for the extract phase and 3.58% for the raffinate phase.

Registry No. Ethanol, 64-17-5; hexanoic acid, 142-62-1; heptanoic acid, 111-14-8; octanoic acid, 124-07-2; nonanoic acid, 112-05-0; phthalic acid diethyl ester, 84-66-2; phthalic acid dibutyl ester, 84-74-2; phthalic acid dioctyl ester, 117-84-0.

Literature Cited

(1) Essien, D.; Pyle, D. L. *Process Biochem.* **1983**, August, 31.
(2) Windholz, M. *The Merck Index*, 10th ed.; Merck: New York, 1983.
(3) Weast, R. C. *Handbook of Chemistry and Physics*, 64th ed.; CRC Press: Cleveland, OH, 1983-84; Section C.
(4) Bottini, Susana B. *J. Chem. Eng. Data* **1986**, *31*, 84-86.
(5) Lyman, W. J.; Reehl, W. F.; Rosenblatt, D. H. *Handbook of Chemical Property Estimation Methods*; McGraw Hill: New York, 1981; Chapter 11-5.
(6) Magnussen, Th.; Rasmussen, P.; Fredenslund, A. *Ind. Eng. Chem. Process. Des. Dev.* **1981**, *20*, 331-339.

Received for review October 20, 1987. Accepted May 6, 1988. We thank the "Junta de Andalucía" for its financial support in this research.

Viscosity of a Mixture of NaSCN and KSCN in Molten Sodium Thiosulfate Pentahydrate. A Case of Positive Deviation from Additivity

Shakira S. Islam and Kochi Ismail*

Department of Chemistry, North-Eastern Hill University, Bijni Campus, Laitumkhrah, Shillong 793 003, India

Density and viscosity data of the molten $0.3[x\text{NaSCN} + (1-x)\text{KSCN}] + 0.7\text{Na}_2\text{S}_2\text{O}_3\cdot5.1\text{H}_2\text{O}$ system are reported as functions of temperature and x. The temperature dependence of viscosity has been described by the Vogel-Tammann-Fulcher equation. A positive deviation of viscosity from additivity has been observed unlike the case with other systems containing mixed alkali-metal ions.

Introduction

In recent years there have been attempts to examine the presence of the mixed alkali effect (MAE) in hydrate melt media (*1-4*). Both electrical conductance and viscosity of mixed alkali systems are found to show, without exception, negative deviation from additivity (*3-7*). However, during our attempt to examine the MAE in the sodium thiosulfate pentahydrate melt we surprisingly observed that in this molten solvent a mixture of sodium and potassium thiocyanates exhibits a positive deviation of viscosity from additivity rather than a negative deviation. Therefore, reported here are the viscosity as well as density data of $0.3[x\text{NaSCN} + (1-x)\text{KSCN}] + 0.7\text{Na}_2\text{S}_2\text{O}_3\cdot5.1\text{H}_2\text{O}$ melt as functions of temperature and x.

Experimental Section

Both NaSCN and KSCN (SD, reagent grade) were recrystallized twice from distilled water and dried over P_2O_5 in a vacuum desiccator. Sodium thiosulfate pentahydrate (S. Merck, GR grade) was used as the solvent in the molten state without further purification. The actual H_2O/Na^+ mole ratio in the sodium thiosulfate pentahydrate sample used was determined to be 5.1 ± 0.01 from iodometric titration. Density and viscosity measurements were made, as described earlier (*8*), in a thermostated water bath. The viscometer constant of the Cannon-Ubbelohde viscometer used in the present work was determined to be 1.294×10^{-3} cm^2·s^{-2}.

Results and Discussion

The measured values of the density are presented in Table I in the form of a linear function of temperature. The experimental values of the viscosity (η) are given in Table II. The non-Arrhenius-type temperature dependence of viscosity was analyzed in terms of the Vogel-Tammann-Fulcher equation of the form

$$\eta = A \exp[B/(T - T_0)] \quad (1)$$

Table I. Parameters of the Density Equation, $\rho = a - bt$ (°C), for $0.3[x\text{NaSCN} + (1-x)\text{KSCN}] + 0.7\text{Na}_2\text{S}_2\text{O}_3\cdot5.1\text{H}_2\text{O}$ Melts

x	a, g·cm^{-3}	10^4b, g·cm^{-3} °C^{-1}	correln coeff
0.0	1.6518	7.2052	−0.987
0.1	1.6509	6.2715	−0.994
0.2	1.6525	6.5545	−0.995
0.4	1.6632	7.4348	−0.998
0.7	1.6586	6.9441	−0.993
0.9	1.6546	6.6019	−0.992
1.0	1.6634	7.1549	−0.995

Table II. Viscosity Data of $0.3[x\text{NaSCN} + (1-x)\text{KSCN}] + 0.7\text{Na}_2\text{S}_2\text{O}_3\cdot5.1\text{H}_2\text{O}$ Melts

	η, cP						
T, K	x = 0.0	x = 0.1	x = 0.2	x = 0.4	x = 0.7	x = 0.9	x = 1.0
294	39.213						
298	31.110		36.986	43.380	42.820	51.933	
303	24.565	27.033	28.185	33.116	36.299	38.977	
308	19.438	21.795	22.563	25.790	28.514	30.126	30.265
313	15.604	17.609	18.140	20.491	22.603	23.281	23.841
318	13.097	14.216	14.859	16.777	18.419	18.924	19.145
323	10.893	11.725	12.041	13.500	14.961	15.255	15.543
328	9.430	9.977	10.271	11.203	12.298	12.711	13.092
333	8.118	8.674	8.809	9.608	10.461	10.804	11.177
338	6.999	7.563	7.583	8.248	9.134	9.229	9.520

Table III. Best-Fit Values of the Parameters of Eq 1 for Viscosity of $0.3[x\text{NaSCN} + (1-x)\text{KSCN}] + 0.7\text{Na}_2\text{S}_2\text{O}_3\cdot5.1\text{H}_2\text{O}$ Melts

x	A, cP	B, K	T_0, K	std dev in ln η
0.0	0.2031	478.68	203.0	0.007
0.1	0.2012	481.35	205.0	0.010
0.2	0.1179	603.49	193.0	0.008
0.4	0.0943	656.41	191.0	0.007
0.7	0.0955	677.47	189.0	0.009
0.9	0.1558	546.48	204.0	0.006
1.0	0.2988	415.76	218.0	0.004

The best-fit values of the three constant parameters, A, B, and T_0, are listed in Table III.

The dependence of η on x is illustrated in Figure 1. From this figure it is apparent that at 308 K there is about 8% positive deviation of η from additivity and the amount of deviation decreases with increase in temperature. At about 338 K and above the viscosity seems to become additive. The deviation of viscosity from additivity, in turn, reveals the existence of MAE. The noteworthy behavior of the present system under study is the positive deviation of η from additivity which is unlike the case observed in all other systems containing mixed alkali-metal

0021-9568/88/1733-0472$01.50/0