Available free online at www.medjchem.com

Mediterranean Journal of Chemistry **2012**, 2(1), 388-400

Relative Permittivity of Carbon Dioxide + Ethanol Mixtures prediction by means of Artificial Neural Networks

Gonzalo Astray *, Manuel A. Iglesias-Otero, Jorge Morales and Juan C. Mejuto

Department of Physical Chemistry, Faculty of Sciences, University of Vigo, 32004, Ourense, Spain.

Abstract: CO_2 + ethanol mixtures have a huge scientific interest and enormous relevance for many industrial processes. Obtaining of their chemical and physical properties is a fundamental task. Relative permittivity (ε_r) of these mixtures is a key property because allows a better knowledge of the structure and the interactions in other media. In this work predictive values of relative permittivity (ε_r) of carbon dioxide + ethanol mixtures were obtained implementing artificial neural networks (ANN_s). They are used successfully in very different fields; therefore it is a very useful tool. In this case the obtained results enhance the ones from the usual multiple linear regression analysis. In both cases mass fraction, pressure and temperature experimental data from a direct capacitance method were used.

Keywords: artificial neural networks, relative permittivity, carbon dioxide, supercritical extraction.

Introduction

In general, the study of the physical properties of binary mixtures of liquids has a huge interest, both scientific and industrial[1-4]. Supercritical carbon dioxide has attracted much attention due to the advantages of having a low critical temperature (T= 304.18 K) and critical pressure (P=7.38 MPa) for being used as a supercritical fluid[5-7]. Furthermore, there are other remarkable aspects like nontoxicity, non-flammability, high purity at low cost and its environmental friendly character. By adding other co solvents, the capacity of extraction of CO_2facing a wider range of compounds can be improved[8-9]. One of these solvents is ethanol. Binary mixtures of carbon dioxide and ethanol have been used successfully in food industry to obtain a varied sort of extracts from feed materials[10-12].

At this point, it is important to know intermolecular interactions and the consequent structural rearrangement of molecules in these processes. This is possible by studying static dielectric constant ε_r (relative permittivity). It is an intrinsic property of materials and accurate values of the pressure and temperature dependence of ε_r carry knowledge about the dynamics of the microstructures[13-14]. In literature there are many examples of studies of that kind, reporting thermodynamic and physical properties of CO_2 + ethanol mixtures[15-17]. The usual procedure to obtain ε_r experimentally involves resources: equipment, materials and time, so it is interesting a method for obtaining that property in function of other parameters by means of predictive methods or simulations.

Experimental results of ε_r in function of temperature and pressure of carbon dioxide + ethanol mixtures, carried out by W. Eltrigham[18] using a direct capacitance method are

**Corresponding author:*
E-mail address: gastray@uvigo.es
DOI: http://dx.doi.org/10.13171/mjc.2.1.2012.10.09.09

obtained in this work by means of Artificial Neural Networks (ANNs). They are a useful tool which have attracted a great deal of attention is several fields, included the prediction of physical properties of chemicals compounds and its mixtures. ANNs are computational-mathematical models based on the structure of biological neural networks, and the human ability of taking decisions. It works learning from real cases and it gives answers when new data are introduced in the case of study.

Experimental section

Data set

Experimental data of relative permittivity (ε_r) of Carbon Dioxide + Ethanol mixtures carried out by W. Eltringham[18] were used in this work (Table 1). They are sets of experimental measures of relative permittivity at different temperatures (303 to 333 K) and pressures (7.2 to 30.8 MPa), carried out at different mass fractions of ethanol.

Table 1. Mass Fraction (ϕ_1) of Ethanol in the Mixture, Temperature (T) and Pressures (P) of experimental mixtures, Relative Permittivity (ε_r) for CO_2 + Ethanol Mixtures, Multiple Lineal Regression values (MLR)and Artificial Neural Networks values (ANN) for Relative Permittivity.

Φ_1	T /K	P /Mpa	$\varepsilon_{r\ exp}$	MLR	ANN	Φ_1	T /K	P /Mpa	$\varepsilon_{r\ exp}$	MLR	ANN
Training											
0.05	303.4	10.0	1.830	1.944	1.802	0.10	322.4	17.1	2.090	2.165	2.123
0.05	303.4	11.4	1.860	1.970	1.836	0.10	322.4	17.6	2.110	2.174	2.134
0.05	303.4	13.2	1.890	2.005	1.868	0.10	322.4	18.6	2.130	2.193	2.154
0.05	303.4	13.6	1.900	2.012	1.874	0.10	322.4	19.6	2.140	2.212	2.171
0.05	303.4	14.8	1.910	2.035	1.890	0.10	322.4	20.6	2.160	2.231	2.187
0.05	303.4	15.3	1.920	2.045	1.896	0.10	322.4	21.6	2.180	2.250	2.201
0.05	303.4	15.8	1.920	2.054	1.901	0.10	322.4	21.7	2.180	2.252	2.202
0.05	303.4	16.0	1.930	2.058	1.903	0.10	322.4	22.6	2.190	2.269	2.213
0.05	303.4	17.5	1.940	2.086	1.919	0.10	322.4	23.6	2.210	2.288	2.225
0.05	303.4	19.2	1.950	2.119	1.936	0.10	322.4	24.5	2.220	2.306	2.235
0.05	303.4	21.0	1.970	2.153	1.954	0.10	322.4	25.5	2.230	2.325	2.245
0.05	303.4	21.3	1.970	2.159	1.957	0.10	322.4	26.5	2.240	2.344	2.255
0.05	303.4	23.0	1.980	2.191	1.975	0.10	322.4	27.5	2.260	2.363	2.264
0.05	303.4	23.3	1.990	2.197	1.978	0.10	322.4	28.4	2.270	2.380	2.272
0.05	303.4	25.1	2.000	2.231	1.999	0.10	322.4	29.9	2.280	2.408	2.284
0.05	303.4	25.4	2.000	2.236	2.003	0.10	333.3	12.9	1.810	1.911	1.751
0.05	303.4	26.7	2.010	2.261	2.019	0.10	333.3	13.7	1.860	1.926	1.811
0.05	303.4	27.2	2.010	2.271	2.025	0.10	333.3	14.8	1.900	1.947	1.881
0.05	303.4	28.9	2.020	2.303	2.048	0.10	333.3	15.7	1.940	1.964	1.929
0.05	303.4	29.6	2.030	2.316	2.057	0.10	333.3	16.7	1.960	1.983	1.973
0.05	313.0	9.8	1.640	1.786	1.640	0.10	333.3	17.8	2.000	2.004	2.014
0.05	313.0	11.3	1.700	1.815	1.694	0.10	333.3	18.5	2.010	2.017	2.036
0.05	313.0	11.7	1.700	1.823	1.706	0.10	333.3	19.4	2.030	2.034	2.060
0.05	313.0	13.2	1.740	1.851	1.742	0.10	333.3	19.6	2.030	2.038	2.065
0.05	313.0	13.7	1.740	1.861	1.751	0.10	333.3	20.6	2.060	2.057	2.088
0.05	313.0	15.7	1.780	1.899	1.779	0.10	333.3	21.7	2.080	2.078	2.110
0.05	313.0	17.4	1.800	1.931	1.795	0.10	333.3	22.6	2.090	2.095	2.127

0.05	313.0	17.5	1.800	1.933	1.796	0.10	333.3	23.9	2.110	2.120	2.147
0.05	313.0	19.2	1.820	1.965	1.808	0.10	333.3	24.8	2.120	2.137	2.161
Φ_1	T /K	P /Mpa	$\varepsilon_{r\ exp}$	MLR	ANN	Φ_1	T /K	P /Mpa	$\varepsilon_{r\ exp}$	MLR	ANN
0.05	313.0	20.7	1.830	1.994	1.818	0.10	333.3	25.2	2.130	2.144	2.166
0.05	313.0	21.6	1.840	2.011	1.823	0.10	333.3	25.6	2.140	2.152	2.172
0.05	313.0	23.5	1.860	2.047	1.834	0.10	333.3	25.6	2.130	2.152	2.172
0.05	313.0	25.3	1.870	2.081	1.845	0.10	333.3	26.6	2.150	2.171	2.185
0.05	313.0	25.4	1.870	2.083	1.845	0.10	333.3	27.2	2.160	2.182	2.192
0.05	313.0	27.4	1.890	2.121	1.858	0.10	333.3	27.5	2.160	2.188	2.196
0.05	313.0	30.4	1.910	2.178	1.880	0.10	333.3	27.9	2.160	2.196	2.201
0.05	322.5	10.2	1.530	1.642	1.528	0.10	333.3	28.5	2.170	2.207	2.207
0.05	322.5	13.1	1.660	1.697	1.664	0.10	333.3	29.2	2.180	2.220	2.215
0.05	322.5	14.2	1.700	1.718	1.699	0.21	303.7	7.2	3.150	3.150	3.200
0.05	322.5	14.7	1.700	1.728	1.712	0.21	303.7	7.9	3.180	3.163	3.225
0.05	322.5	16.0	1.730	1.752	1.739	0.21	303.7	8.8	3.220	3.180	3.255
0.05	322.5	16.1	1.730	1.754	1.741	0.21	303.7	9.8	3.250	3.199	3.284
0.05	322.5	18.9	1.780	1.807	1.777	0.21	303.7	13.0	3.350	3.260	3.364
0.05	322.5	19.5	1.790	1.819	1.782	0.21	303.7	14.9	3.400	3.296	3.406
0.05	322.5	20.8	1.800	1.843	1.792	0.21	303.7	15.0	3.400	3.298	3.408
0.05	322.5	21.8	1.810	1.862	1.798	0.21	303.7	16.5	3.440	3.327	3.440
0.05	322.5	22.7	1.820	1.880	1.803	0.21	303.7	16.7	3.450	3.331	3.444
0.05	322.5	23.6	1.830	1.897	1.807	0.21	303.7	17.3	3.460	3.342	3.457
0.05	322.5	25.8	1.850	1.938	1.818	0.21	303.7	18.0	3.470	3.355	3.472
0.05	322.5	26.3	1.860	1.948	1.820	0.21	303.7	18.8	3.490	3.370	3.488
0.05	322.5	27.9	1.870	1.978	1.828	0.21	303.7	20.2	3.520	3.397	3.517
0.05	322.5	28.4	1.870	1.988	1.830	0.21	303.7	21.6	3.540	3.424	3.546
0.05	322.5	29.3	1.880	2.005	1.835	0.21	303.7	21.8	3.550	3.427	3.550
0.05	322.5	30.3	1.890	2.024	1.840	0.21	303.7	23.3	3.570	3.456	3.578
0.05	333.2	10.5	1.320	1.477	1.390	0.21	303.7	23.9	3.580	3.467	3.589
0.05	333.2	11.2	1.410	1.490	1.423	0.21	303.7	25.4	3.610	3.496	3.614
0.05	333.2	12.1	1.480	1.507	1.471	0.21	303.7	26.2	3.620	3.511	3.626
0.05	333.2	13.0	1.530	1.524	1.521	0.21	303.7	27.2	3.640	3.530	3.639
0.05	333.2	13.7	1.570	1.537	1.558	0.21	303.7	28.4	3.660	3.553	3.652
0.05	333.2	14.9	1.620	1.560	1.616	0.21	303.7	30.2	3.680	3.587	3.666
0.05	333.2	17.0	1.670	1.600	1.691	0.21	312.8	8.0	2.800	3.020	2.830
0.05	333.2	17.6	1.690	1.611	1.707	0.21	312.8	9.3	2.860	3.044	2.898
0.05	333.2	19.1	1.720	1.640	1.737	0.21	312.8	11.2	2.940	3.080	2.975
0.05	333.2	21.0	1.750	1.676	1.762	0.21	312.8	11.5	2.940	3.086	2.986
0.05	333.2	21.6	1.750	1.687	1.768	0.21	312.8	14.2	3.000	3.137	3.068
0.05	333.2	22.9	1.770	1.712	1.778	0.21	312.8	14.3	3.010	3.139	3.071
0.05	333.2	23.7	1.780	1.727	1.783	0.21	312.8	14.9	3.030	3.151	3.087
0.05	333.2	26.9	1.820	1.788	1.798	0.21	312.8	15.8	3.050	3.168	3.109
0.05	333.2	27.4	1.820	1.798	1.800	0.21	312.8	18.0	3.140	3.210	3.160
0.05	333.2	28.8	1.830	1.824	1.805	0.21	312.8	20.0	3.170	3.248	3.202
0.05	333.2	29.9	1.840	1.845	1.809	0.21	312.8	20.6	3.180	3.259	3.214
0.10	303.7	9.8	2.240	2.325	2.237	0.21	312.8	22.2	3.220	3.289	3.244
0.10	303.7	11.3	2.270	2.354	2.285	0.21	312.8	22.8	3.230	3.301	3.255

0.10	303.7	11.4	2.280	2.356	2.288	0.21	312.8	23.7	3.250	3.318	3.271
0.10	303.7	13.1	2.300	2.388	2.329	0.21	312.8	26.3	3.300	3.367	3.314
Φ_1	T /K	P /Mpa	$\varepsilon_{r\ exp}$	MLR	ANN	Φ_1	T /K	P /Mpa	$\varepsilon_{r\ exp}$	MLR	ANN
0.10	303.7	14.9	2.340	2.422	2.363	0.21	312.8	28.1	3.320	3.402	3.344
0.10	303.7	16.0	2.360	2.443	2.380	0.21	312.8	28.4	3.340	3.407	3.349
0.10	303.7	16.9	2.370	2.460	2.393	0.21	312.8	30.8	3.370	3.453	3.389
0.10	303.7	17.8	2.380	2.477	2.406	0.21	323.4	9.8	2.590	2.884	2.578
0.10	303.7	19.1	2.400	2.502	2.422	0.21	323.4	10.6	2.610	2.899	2.630
0.10	303.7	19.1	2.400	2.502	2.422	0.21	323.4	11.5	2.670	2.917	2.680
0.10	303.7	19.9	2.410	2.517	2.432	0.21	323.4	13.1	2.750	2.947	2.752
0.10	303.7	20.4	2.420	2.527	2.438	0.21	323.4	14.1	2.790	2.966	2.790
0.10	303.7	21.4	2.430	2.546	2.449	0.21	323.4	15.8	2.850	2.998	2.848
0.10	303.7	21.9	2.430	2.555	2.454	0.21	323.4	16.6	2.870	3.013	2.873
0.10	303.7	23.1	2.450	2.578	2.467	0.21	323.4	17.8	2.900	3.036	2.908
0.10	303.7	24.2	2.460	2.599	2.479	0.21	323.4	19.6	2.950	3.070	2.958
0.10	303.7	25.3	2.470	2.620	2.490	0.21	323.4	19.7	2.950	3.072	2.961
0.10	303.7	25.5	2.480	2.624	2.492	0.21	323.4	21.1	2.980	3.099	2.998
0.10	303.7	25.5	2.480	2.624	2.492	0.21	323.4	22.9	3.030	3.133	3.043
0.10	303.7	26.5	2.480	2.643	2.502	0.21	323.4	23.1	3.030	3.137	3.047
0.10	303.7	28.0	2.500	2.671	2.517	0.21	323.4	23.2	3.030	3.139	3.050
0.10	303.7	28.4	2.500	2.679	2.521	0.21	323.4	24.7	3.060	3.167	3.085
0.10	303.7	29.4	2.510	2.698	2.531	0.21	323.4	26.0	3.080	3.192	3.114
0.10	313.1	10.2	2.000	2.183	2.010	0.21	323.4	26.7	3.100	3.205	3.128
0.10	313.1	11.0	2.030	2.198	2.048	0.21	323.4	27.9	3.120	3.228	3.153
0.10	313.1	12.0	2.050	2.217	2.088	0.21	323.4	29.5	3.140	3.259	3.183
0.10	313.1	12.7	2.080	2.230	2.112	0.21	323.4	30.6	3.150	3.279	3.203
0.10	313.1	13.1	2.090	2.238	2.124	0.21	333.2	11.9	2.380	2.767	2.411
0.10	313.1	13.7	2.110	2.249	2.140	0.21	333.2	12.9	2.450	2.786	2.476
0.10	313.1	14.8	2.130	2.270	2.166	0.21	333.2	13.2	2.470	2.792	2.493
0.10	313.1	17.0	2.170	2.312	2.206	0.21	333.2	14.1	2.520	2.809	2.538
0.10	313.1	17.7	2.180	2.325	2.216	0.21	333.2	14.7	2.540	2.821	2.565
0.10	313.1	18.8	2.190	2.346	2.231	0.21	333.2	15.8	2.590	2.841	2.607
0.10	313.1	19.8	2.200	2.365	2.243	0.21	333.2	16.2	2.610	2.849	2.621
0.10	313.1	22.1	2.230	2.409	2.267	0.21	333.2	16.9	2.620	2.862	2.644
0.10	313.1	22.4	2.240	2.414	2.270	0.21	333.2	17.3	2.640	2.870	2.657
0.10	313.1	24.1	2.260	2.447	2.285	0.21	333.2	18.5	2.680	2.893	2.692
0.10	313.1	24.4	2.260	2.452	2.288	0.21	333.2	19.1	2.700	2.904	2.709
0.10	313.1	25.8	2.280	2.479	2.299	0.21	333.2	19.2	2.700	2.906	2.712
0.10	313.1	26.4	2.280	2.490	2.303	0.21	333.2	21.2	2.750	2.944	2.765
0.10	313.1	27.7	2.300	2.515	2.313	0.21	333.2	21.2	2.750	2.944	2.765
0.10	313.1	27.8	2.300	2.517	2.313	0.21	333.2	21.2	2.750	2.944	2.765
0.10	313.1	28.3	2.300	2.527	2.317	0.21	333.2	21.3	2.750	2.946	2.768
0.10	313.1	29.3	2.310	2.546	2.324	0.21	333.2	23.0	2.790	2.978	2.812
0.10	313.1	29.5	2.320	2.549	2.325	0.21	333.2	23.1	2.790	2.980	2.815
0.10	322.4	10.5	1.860	2.040	1.831	0.21	333.2	24.9	2.830	3.014	2.862
0.10	322.4	11.9	1.940	2.066	1.927	0.21	333.2	25.0	2.830	3.016	2.864
0.10	322.4	11.9	1.940	2.066	1.927	0.21	333.2	25.2	2.830	3.020	2.869

0.10	322.4	12.2	1.960	2.072	1.944	0.21	333.2	25.5	2.850	3.026	2.877
0.10	322.4	13.7	2.010	2.100	2.018	0.21	333.2	26.8	2.860	3.050	2.911
Φ_1	T /K	P /Mpa	$\varepsilon_{r\ exp}$	MLR	ANN	Φ_1	T /K	P /Mpa	$\varepsilon_{r\ exp}$	MLR	ANN
0.10	322.4	15.7	2.060	2.138	2.087	0.21	333.2	27.0	2.870	3.054	2.916
0.10	322.4	15.7	2.060	2.138	2.087	0.21	333.2	28.4	2.900	3.081	2.952
0.10	322.4	15.8	2.070	2.140	2.090	0.21	333.2	30.6	2.940	3.123	3.006
Validation 1											
0.05	303.4	19.0	1.950	2.115	1.934	0.10	303.7	14.0	2.320	2.405	2.347
0.05	313.0	9.7	1.630	1.785	1.636	0.10	303.7	24.1	2.460	2.597	2.478
0.05	313.0	9.9	1.650	1.788	1.644	0.10	303.7	27.4	2.490	2.660	2.511
0.05	313.0	11.8	1.700	1.824	1.709	0.10	313.1	9.7	1.980	2.173	1.983
0.05	313.0	15.1	1.770	1.887	1.772	0.10	313.1	15.8	2.150	2.289	2.186
0.05	313.0	17.5	1.800	1.933	1.796	0.10	313.1	21.9	2.230	2.405	2.265
0.05	322.5	12.1	1.630	1.678	1.624	0.10	322.4	13.9	2.020	2.104	2.026
0.05	322.5	17.2	1.750	1.775	1.758	0.10	322.4	16.7	2.090	2.157	2.114
0.05	322.5	24.7	1.840	1.918	1.812	0.10	333.3	11.9	1.740	1.892	1.668
0.05	322.5	29.5	1.880	2.009	1.836	0.10	333.3	26.5	2.150	2.169	2.184
0.05	333.2	13.0	1.540	1.524	1.521	0.21	303.7	11.0	3.290	3.222	3.316
0.05	333.2	15.9	1.640	1.579	1.656	0.21	312.8	17.4	3.110	3.198	3.147
0.05	333.2	19.4	1.720	1.646	1.742	0.21	323.4	12.4	2.710	2.934	2.722
0.05	333.2	25.0	1.800	1.752	1.790	0.21	323.4	18.8	2.930	3.055	2.936
Validation 2											
0.15	304.9	16.1	2.670	2.832	2.578	0.15	323.3	9.9	2.060	2.420	2.142
0.15	304.9	16.8	2.680	2.845	2.589	0.15	323.3	11.0	2.130	2.440	2.213
0.15	304.9	17.3	2.680	2.855	2.597	0.15	323.3	12.0	2.180	2.459	2.262
0.15	304.9	17.8	2.690	2.864	2.605	0.15	323.3	12.7	2.210	2.473	2.289
0.15	304.9	18.8	2.700	2.883	2.621	0.15	323.3	13.6	2.250	2.490	2.317
0.15	304.9	19.4	2.720	2.894	2.631	0.15	323.3	14.7	2.280	2.511	2.343
0.15	304.9	20.1	2.730	2.908	2.644	0.15	323.3	15.9	2.310	2.534	2.364
0.15	304.9	20.8	2.740	2.921	2.656	0.15	323.3	16.9	2.340	2.553	2.377
0.15	304.9	21.9	2.750	2.942	2.677	0.15	323.3	17.8	2.360	2.570	2.388
0.15	304.9	22.8	2.760	2.959	2.695	0.15	323.3	18.6	2.370	2.585	2.395
0.15	304.9	23.7	2.770	2.976	2.713	0.15	323.3	18.7	2.380	2.587	2.396
0.15	304.9	24.3	2.790	2.988	2.726	0.15	323.3	19.5	2.400	2.602	2.403
0.15	304.9	24.7	2.780	2.995	2.735	0.15	323.3	20.3	2.410	2.617	2.409
0.15	304.9	25.5	2.790	3.010	2.753	0.15	323.3	21.7	2.440	2.644	2.419
0.15	304.9	26.4	2.810	3.027	2.774	0.15	323.3	22.8	2.450	2.665	2.426
0.15	304.9	26.5	2.810	3.029	2.777	0.15	323.3	23.1	2.460	2.670	2.428
0.15	304.9	27.2	2.820	3.043	2.794	0.15	323.3	23.5	2.470	2.678	2.431
0.15	304.9	27.2	2.820	3.043	2.794	0.15	323.3	24.5	2.480	2.697	2.438
0.15	304.9	28.2	2.830	3.062	2.819	0.15	323.3	25.4	2.500	2.714	2.444
0.15	304.9	29.1	2.840	3.079	2.843	0.15	323.3	26.5	2.510	2.735	2.452
0.15	304.9	29.8	2.850	3.092	2.863	0.15	323.3	28.4	2.540	2.771	2.466
0.15	313.1	10.1	2.370	2.587	2.317	0.15	323.3	29.5	2.560	2.792	2.475
0.15	313.1	10.9	2.390	2.602	2.343	0.15	333.3	11.8	1.990	2.296	2.062
0.15	313.1	11.8	2.420	2.619	2.366	0.15	333.3	12.9	2.070	2.317	2.150
0.15	313.1	12.7	2.450	2.636	2.384	0.15	333.3	13.8	2.110	2.334	2.205

0.15	313.1	13.8	2.470	2.657	2.403	0.15	333.3	14.8	2.160	2.353	2.252
0.15	313.1	14.6	2.490	2.672	2.414	0.15	333.3	15.9	2.200	2.374	2.290
Φ_1	T /K	P /Mpa	$\varepsilon_{r\ exp}$	MLR	ANN	Φ_1	T /K	P /Mpa	$\varepsilon_{r\ exp}$	MLR	ANN
0.15	313.1	15.7	2.520	2.693	2.428	0.15	333.3	16.7	2.220	2.389	2.311
0.15	313.1	16.8	2.540	2.714	2.440	0.15	333.3	17.7	2.260	2.408	2.332
0.15	313.1	17.8	2.560	2.733	2.450	0.15	333.3	18.7	2.280	2.427	2.348
0.15	313.1	18.8	2.580	2.752	2.460	0.15	333.3	19.7	2.310	2.446	2.360
0.15	313.1	19.5	2.590	2.765	2.467	0.15	333.3	20.8	2.330	2.467	2.371
0.15	313.1	20.8	2.610	2.790	2.480	0.15	333.3	22.0	2.360	2.489	2.380
0.15	313.1	21.6	2.620	2.805	2.489	0.15	333.3	22.7	2.370	2.503	2.384
0.15	313.1	22.6	2.630	2.824	2.500	0.15	333.3	23.5	2.380	2.518	2.389
0.15	313.1	23.5	2.640	2.841	2.510	0.15	333.3	24.5	2.400	2.537	2.394
0.15	313.1	24.5	2.660	2.860	2.522	0.15	333.3	25.6	2.420	2.558	2.400
0.15	313.1	25.5	2.670	2.879	2.534	0.15	333.3	26.6	2.430	2.577	2.404
0.15	313.1	26.5	2.680	2.898	2.548	0.15	333.3	27.6	2.450	2.596	2.409
0.15	313.1	27.5	2.690	2.917	2.562	0.15	333.3	28.4	2.460	2.611	2.412
0.15	313.1	27.9	2.700	2.925	2.568	0.15	333.3	29.2	2.470	2.626	2.416
0.15	313.1	28.4	2.710	2.934	2.575	0.15	333.3	29.9	2.480	2.640	2.419
0.15	313.1	29.3	2.720	2.951	2.589						

The procedure to forecast some values by means of other consist of use a set of data to develop the model (training) and use some different to test it (validation). In this work we used 248 cases for training and 113 cases for validation. Two different subsets of data were taken for validation. One with similar values to the ones used in training (called validation 1, 28 cases) and other with a little bit different values (validation 2, 85 cases).

Multilinear Regression Analysis (MLRA)

In the study of physicochemical properties of chemical compounds and their mixtures, multilinear regression analysis (MLRA) is a common primary tool for a first or previous examination of data[19] (Equation 1). IBM SPSS Statistics v.19 was used in this work MLRA was used in order to obtain ε_r values from the other variables involved, in this way:

$$\varepsilon_r = a_0 + a_1\phi + a_2T + a_3P \qquad (1)$$

The operating method was to use a subset of data including values of the four variables for obtaining a_1 coefficients (training process) and after that try to obtain ε_r using those coefficients and new ϕ, P and T values (validation process).

Artificial Neural Network (ANN)

Artificial Neural Networks are a set of mathematical, statistical and computational methods based on the human brain and its way of work by means of biological neural networks[20-22]. An Artificial Neural Network uses a high number of units (neurons) interconnected among them by using a connectionist approach to computation. They are needed sets of data, which are differenced in inputs and outputs. The way of using ANNs has two parts. One is called training, and as the own word says, it consists on a process where the system is able to identify the different inputs with the outputs, and in definitive, their relations. It is said that the system is, in certain way, “learning”. In the second part, (validation), the ANN provides an output when new inputs are introduced. This answer is based on the information that the own system was able to catch in training part. New outputs will be correct if the inputs used for training and validation are similar. They have been used successfully in several fields, apart from physical chemical characterization[23], from economy[24] to biological[25-26] or environmental issues[27-28]. Explained more formally, the information collected by a vector (Equation 2) is propagated to the first intermediate layer by a function called spread function, and its mission is to add all the excitatory signals that reach neuron (Equation 3). N is the number of neurons in the input layer, w_{ji} is the value of the weight between the input neuron i and the intermediate neuron j and b_j is the value of the bias neuron associated to the neuron j of the intermediate layer.

$$X = (X_1, X_2, ..., X_n) \qquad (2)$$

$$S_j = \sum_{i=1}^{N} W_{ji} X_i + b_j \qquad (3)$$

Activation function treats the generated value and generates an excitatory answer to signals received (Equation 4). Although they are available different activations functions depending on the kind of problem to solve, in this case the activation function chosen is the sigmoidal (Equation 5).

$$Y_j = F_j(S_j) \qquad (4)$$

$$F(Z) = \frac{1}{1+e^{-Z}} \qquad (5)$$

It is because it is widely recommended in the literature and it has been used previously with success[20-23]. The information attains the last neuron, and then the spawned value is checked with the experimental value (Equation 6) to establish an error value. This is used in order to determine the end of the training part.

$$E = \frac{1}{2}\sum_{K=1}^{P} (d_K - y_K)^2 \qquad (6)$$

Modelization

Several tests were carried out modifying the architectures of ANN for forecasting relative permittivity of carbon dioxide + ethanol mixtures. The tests consisted of carry out different calculus with different number of cycles, modifying the level of accepted error, modifying the number of layers and the variables used in each one. The intention was to optimise the labour in terms of time and memory spending. The neural networks were developed with three neurons in the input layer, corresponding to temperature, mass fraction of the first compound and pressure, and output layer with one neuron, corresponding to relative permittivity, and a variable number of intermediate layers, which was assayed taking into account the number of neurons, distributed in these layers by eq. 7.

$$\frac{M}{2N} < n < \frac{2M}{N} \qquad (7)$$

M designates the number of training cases, N the number of input variables and n the number of neurons in the intermediate layers. To clearly differentiate all neural networks, they are named using this notation: $N_{in} - [N_{int1} - N_{int2} - N_{int3}]_e - N_{out}$ where N_{in} and N_{out} are the number of neurons in the input and output layer, respectively. N_{int1}, N_{int2} and N_{int3} correspond with the number of neurons in the intermediate layers; in the case of they were implemented (Figure 1).

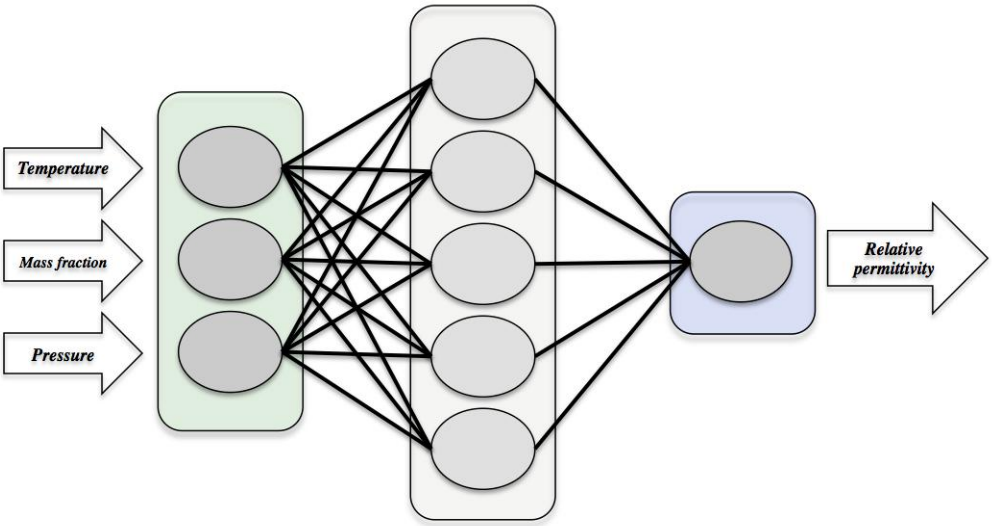

Fig. 1. Artificial Neural Network with an input layer with three neurons, one hidden layer with five neurons and one input layer with one neuron.

Results and Discussion

Multilinear Regression Analysis (MLRA)

As it was already said, experimental data were obtained by a direct capacitance method. The variables involved were three: mass fraction of one of the compounds of the binary mixtures, pressure ant temperature. In Table 1 it can be seen the used values, separated To develop a multiple lineal regression analysis the first step consist of carry out a statistical analysis of the data in terms of Pearson correlation.

As it is seen in Table 2, the used variables for forecasting ε_r (mass fraction, temperature and pressure) are not linearly dependent among them.

Table 2. Coefficients of Pearson correlation among four variables involved.

	Mass fraction	**Temperature /K**	**Pressure / MPa**	**ε_r**
Mass fraction	1			
Temperature/K	0.032	1		
Pressure /Mpa	0.002	0.036	1	
ε_r	0.894	-0.310	0.210	1

Relative permittivity posses a significant correlation respect to mass fraction of one of the compounds of the binary mixtures, pressure ant temperature. Table 3 shows obtained results for training data using Equation 1.

Table 3. Fitting parameters and standard deviations for MRLA using eq.1.

	Parameter	**Standard Error**
Constant	6.218	0.182
Mass fraction	7.804	0.097
Temperature / K	-0.016	0.001
Pressure / Mpa	0.019	0.001

Root mean square error (RMSE) values, given by:

$$RMSE = \sqrt{\sum_{i=1}^{N} \frac{\left(\varepsilon_i^{pred} - \varepsilon_i^{real}\right)^2}{N}} \qquad (8)$$

and individual percent deviation (IPD), obtained in this way:

$$IPD = 100 \times \left(\frac{\varepsilon_i^{pred} - \varepsilon_i^{real}}{\varepsilon_i^{real}} \right) \qquad (9)$$

are commonly accepted to evaluate the accuracy of predicted data[29].

Table 4 shows coefficient R^2 values of linear correlation between predicted and experimental values together with RMSE and average IPD values.

Table 4. Correlation coefficient (R^2) and Root Mean Square Error values (RMSE) for training (T) and validation parts (V), validations 1 and 2 for MLRA.

	R^2_T	$RMSE_T$	R^2_V	$RMSE_V$	R^2_{V1}	$RMSE_{V1}$	R^2_{V2}	$RMSE_{V2}$
	0.967	0.143	0.969	0.187	0.971	0.121	0.964	0.204
Error (%)		5.316		7.386		5.334		8.062

Subscript *T* denotes training cases and V1 and V2 denotes the two groups of validation data, cited above. For training data, MLRA gives a high level of correlation R^2 (0.967), with a low value of RMSE (0.143), with a correspondent average IPD value of 5.3% (Figure 2). But the importance of this method lies in the behaviour with data more or less different from the ones used in training part.

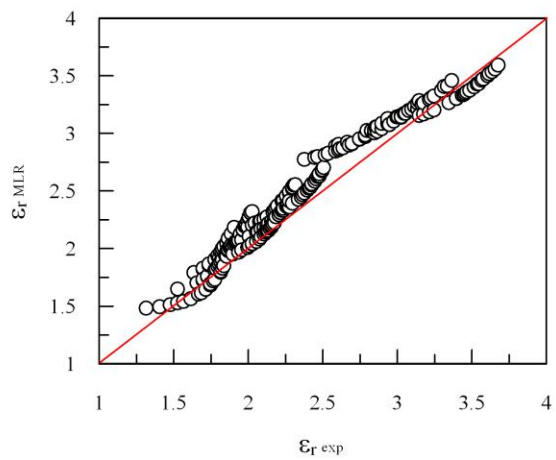

Fig. 2. Experimental vs. calculated value of Relative Permittivity (ε_r) for training phase by MLRA model.

When validation was carried out using all data destined to it (Table 1), a good correlation between predicted and experimental ε_r was obtained (R^2=0.969) with RMSE=0.187 and average IPD value of 7.4%. Validation 1 was done taking values similar to the ones used in training part. In this case there is a good predicted-experimental correlation, slightly better than the one made using all validation values (see Table 1). Validation 2, carried out with input values significantly different, gives relatively good results. Predictive values posses a correlation with the experimental ones of R^2=0.964 and a RMSE=0.204; expressed in terms of average IPD, 8.06% (Figures 3-4).

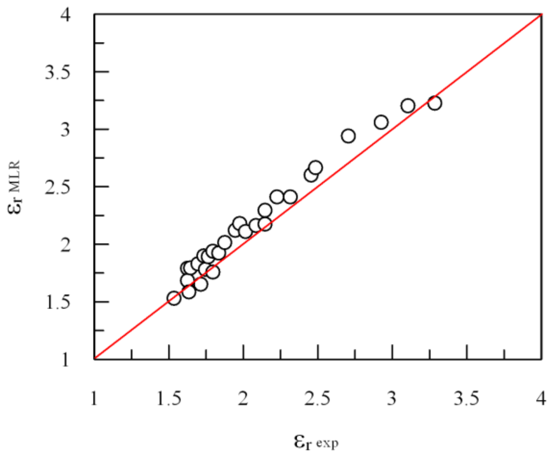

Fig. 3. Experimental vs. calculated value of Relative Permittivity (ε_r) for validation 1 by MLRA model.

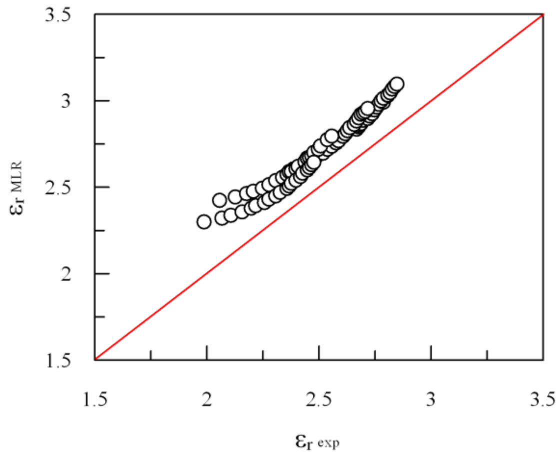

Fig. 4. Experimental vs. calculated value of Relative Permittivity (ε_r) for validation 2 by MLRA model.

It seems that MLRA provides good results but it is possible that using input data quite different from the ones used in training, average IPD should increase, then MLRA, obviously, is not the best option for forecasting ε_r . MLRA method can be good if very good accuracy is not vital but ANN method provides much more refined values.

ANN

It has tried to enhance predictive results of ε_r by using ANNs. Although it was said that neural networks are used commonly in non-linear situations[30], it is not the case. Even so, ANNs were implemented.

With ANN, there were used the same input variables and the same training and validation data than in MRLA method in order to make a comparative study between both predictive models.

In Table 5 are shown, ordered by total RMSE (RMSE of training part + RMSE of validation part), the best five neural networks with the correspondent fitting parameter R^2 of predicted and experimental ε_r.

Table 5. Correlation coefficient (R^2) and Root Mean Square Errors (RMSE) for training (T), validation phase (V) and sum for ANN.

Topology	R^2_T	$RMSE_T$	R^2_V	$RMSE_V$	$RMSE_{sum}$
3-5-1	0.999	0.026	0.970	0.067	0.093
3-7-2-1	1.000	0.010	0.949	0.117	0.127
3-4-4-1	0.999	0.019	0.908	0.109	0.128
3-7-3-1	1.000	0.008	0.926	0.121	0.129
3-5-1-1	0.995	0.053	0.952	0.080	0.133

According to this, 3-5-1 topology supplies the best result. For training data, as it was expected, obtained results are good (Figure 5). But, the most important is the result obtained in validation part, and more specifically the validation part where input data are quite different that the ones used for train the neural network.

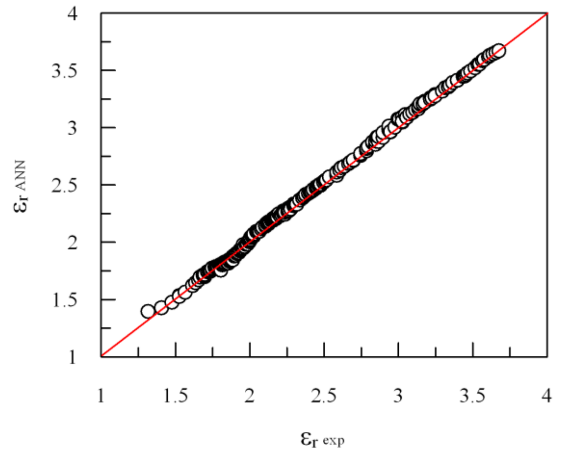

Fig. 5. Experimental vs. calculated value of Relative Permittivity (ε_r) for training phase by ANN model.

In Table 6 are shown results of R^2 correlation coefficient for predicted and experimental values, RMSE values and average IPD.

Table 6. Correlation coefficient (R^2) and Root Mean Square Error values (RMSE) for training (T) and validation parts (V), validations 1 and 2 for ANN with topology 3-5-1.

	R^2_T	$RMSE_T$	R^2_V	$RMSE_V$	R^2_{V1}	$RMSE_{V1}$	R^2_{V2}	$RMSE_{V2}$
	0.999	0.026	0.970	0.067	0.998	0.025	0.922	0.076
Error (%)		0.948		2.237		0.963		2.666

R^2 correlation coefficients are in all cases greater than 0.9, but the main important is that RMSE values are less than the ones obtained with MLRA method, both for the two groups of validation data (Figures 6-7).

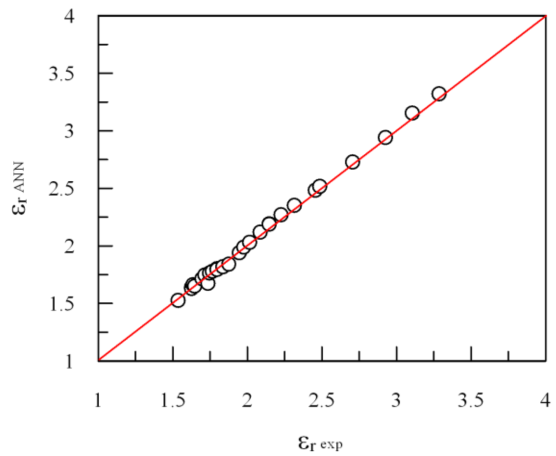

Fig. 6. Experimental vs. calculated value of Relative Permittivity (ε_r) for validation 1 by ANN model.

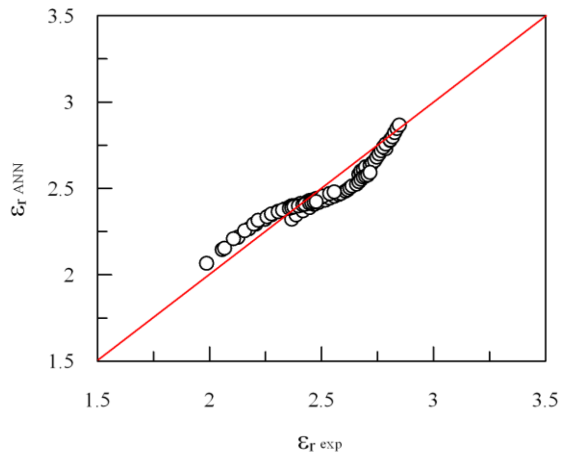

Fig. 7. Experimental vs. calculated value of Relative Permittivity (ε_r) for validation 2 by ANN model.

Specifically for the cases of validation 2, whose data are quite different from training data, ANN provides good results too. R^2 value of 0.922, RMSE of 0.076 and expressed in average IPD, 2.67%. It represents an enhancement in terms of percentage of around 62% by using ANN respect to use MRLA. In this case, ANN predictive model furnishes good results, obtained easily and quickly.

Conclusion

Relative permittivity of binary mixtures of Carbon Dioxide + Ethanol were obtained using artificial neural networks (ANNs) my means of three variable values involved in a previous work, that reported data by means of a direct capacitance method. In this work it was verified that MLRA could forecast in certain way relative permittivity values with good reliability, nevertheless ANN predictive model enhances results from this model significantly. This work proves once more the availability of artificial neural networks to obtain predictive values of some physical properties by means of the other ones, previously obtained. By using ANN`s accurate predictive values of chemical and physical properties can be obtained with lower cost than if they must be obtained experimentally.

Acknowledgements

Astray thanks "Ministerio de Educación" of Spain for a FPU. Iglesias-Otero and Morales thank University of Vigo for a research-training grant.

References

1. F. S. Oliveira, M.G. Freire, P.J. Carvalho, J.A.P. Coutinho, J.N. Canongia-Lopes, L.P.N. Rebelo, I.M. Marrucho. J. Chem. Eng. Data, **2010**, 55, 4514-4520.
2. B. González, E. J. González, I. Domínguez, A. Domínguez. Phys. Chem. Liq., **2010**, 48, 514-533.
3. B. Mokhtarani, A. Sharifi, H. R. Mortaheb, M. Mirzae, M. Mafi, F. Sadeghian, F. J. Chem. Thermodynamics, **2009**, 41, 323-329.
4. F. X. Feitosa, M. L. Rodrigues, C.B. Veloso, L. CeLio, L.J. Cavalcante, M.C.G. Albuquerque, H. B. De Sant'Ana. J. Chem. Eng. Data, **2010**, 55, 3909-3914.
5. L.A. Blanchard, J.F. Brennecke. Ind. Eng. Chem. Res., **2010**, 40, 287-292.
6. J.L. Kendall, D.A. Canelas, J.L. Young, J.M. DeSimone. Chem. Rev., **1999**, 99, 543-563.
7. W. Leitner. Acc. Chem. Res., **2002**, 35, 746-756.
8. L. Teberikler, S. Koseoglu, A. Akgerman. J. Am. Oil Chem. Soc., **2001**, 78, 115-120.
9. J. Ke, C.Mao, M. Zhong, B. Han, H. Yan. J. Supercrit. Fluid., **1996**, 9, 82-87.
10. S.S.T. Ting, D. L. Tomasko, N.R. Foster, S. J. Macnaughton. Ind. Eng. Chem. Res., **1993**, 32, 1471-1481.
11. M. D. Saldaña, C. Zetzl, R. S. Mohamed, G. Brunner. J. Agric. Food Chem., **2002**, 50, 4820-4826.
12. T. Baysal, S. Ersus, D. A. J. Starmans. J. Agric. Food Chem., **2000**, 48, 5507-5511.
13. O. Teschke, G. Ceotto, E.F. De Souza.. Phys. Chem. Chem. Phys., **2001**, 3, 3761-3768.
14. G. C. Franchini, A. Marchetti, M. Tagliazucchi, L. Tassi, G. Tosi. J. Chem. Soc. Faraday Trans., **1991**, 87, 2583-2588.
15. C. J. Chang, C. Y. Day, C. M. Ko, K. L. Chiu. Fluid Phase Equilibr., **1997**, 131, 243-258.
16. Z. Sun, X. Zhang, B. Han, Y. Wu, G. An, Z. Liu, S. Miao, Z. Miao. Carbon **2007**, 45, 2589–2596.
17. B. S. Chun, T. Gordon, T. Wilkinson. Ind. Eng. Chem. Res., **1995**, 34, 4371-4377.
18. W. Eltringham. J. Chem. Eng. Data, **2011**, 56, 3363-3366.

19. L. Jared, J. D. Anderson, T. Welton. D. W. Armstrong. J. Am. Chem. Soc., **2002**, 124, 14247-14254.
20. S. Haykin. Neural Networks: A comprehensive foundation; Prentice Hall: New Jersey, **2008**.
21. J. R. Hilera, V.J. Martíne. Redes neuronales artificiales. Fundamentos, modelos y aplicaciones; Addisson-Wesley Iberoamericana S.A.: Madrid, **1995**.
22. S. Haykin. Neural Networks and Learning Machines; Pearson Prentice Hall: New Jersey, **2009**.
23. G. Astray, P. V. Caderno, J. A. Ferreiro-Lage, J. F. Galvez, J. C. Mejuto. J. Chem. Eng. Data **2010**, 55, 3542-3547.
24. R. W. Janson, C. Batur, L. Krishna. Ohio J. Sci., **2001**, 101, 57-64.
25. G. Astray, F. J. Rodríguez-Rajo, J.A. Ferreiro-Lage, J.A. Fernández-González, M.V. Jato, J.C. Mejuto. J. Environ. Monitoring, **2010**, 12, 2145-2152.
26. G. Astray, J. X. Castillo, J.A. Ferreiro-Lage, J.F. Galvez, J.C. Mejuto. Cienc. Tecnol. Aliment., **2010**, 8, 79.
27. H.R. Maier, G.C. Dandy. Environ. Mod. Soft. **2000**, 15, 101-124.
28. P. Araujo, G. Astray, A. Cid, A. Orosa, O. Moldes, B. Soto, J.A. Rodríguez-Suarez. Electron. J. Environ. Agric. Food Chem., **2011**, 10, 1608-1615.
29. A. Habibi-Yangjeh. Phys. Chem. Liq, **2007**, 4, 471-478.
30. I. Rivals, L. Personnaz. IEEE Trans. Neural Networks, **2000**, 24, 9-10.