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EXCESS MOLAR VOLUMES AND PARTIAL MOLAR VOLUMES FOR BINARY MIXTURES PROPANOIC ACID WITH 1-PROPANOL, 2-PROPANOL, 1-BUTANOL AND 1-PENTANOL

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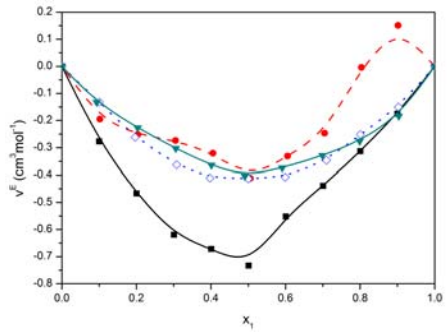
The densities of binary acid - alcohol mixtures were determined experimentally by the pycnometer method for four binary systems: propanoic acid with 1-propanol, 2-propanol, 1-butanol and 1-pentanol at 298,15K. From the experimental data, excess molar volumes and partial molar volumes were calculated. The partial molar volumes were revealed by the intersection method and the excess molar volumes were fitted using the polynomial equations of Redlich-Kister type. The results indicate the presence of attractive forces between the components and the decrease of the hydrogen bond strength as the length of the alcohol chain increases.



INTRODUCTION

The thermodynamic characterization of binary systems can be done using thermodynamic properties such as volume, enthalpy, Gibbs free energy, entropy. The thermodynamic excess functions, introduced by Raymond and Scatchard, are quantities that show the deviation from ideal behavior, adapted to the treatment of non-ideal solutions, as well as of a component of such a solution. Excess thermodynamic functions and partial molar quantities are fundamental in the characterization of real systems. With the help of the excess functions it is possible to evaluate the behavior when mixing two miscible components in any proportion. In the case of binary mixtures of liquids, the excess molar volume is used to determine the nature and type of the interactions that take place in the system and can be calculated directly from density measurements.

This work is therefore aimed at determination of excess molar volumes and partial molar volumes in the binary mixtures of 1-propanol, 2-propanol, 1-butanol and 1-pentanol with propanoic acid at 25^{o}C. In addition, the influence of the structure of the alcohol on the excess molar volume, having the same component 1 (propanoic acid) in all systems, was tracked.

Propanoic acid is found in several foods, such as milk, yogurt and cheese.[1] It is also used as a preservative (E280) because it has antibacterial and antifungal effects. Undigested foods are fermented in the colon and give rise to metabolites, among these metabolites was propanoic acid. Propanoic acid is beneficial to the human body because it lowers fatty acids in the liver, reduces food intake, prevents obesity and type 2 diabetes by improving insulin sensitivity.[2-4] 1-propanol was first discovered in 1853 by Gustave Charles Bonaventure Chancel[5] and is used as a fuel because it is a flammable liquid.[6]

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2-propanol is the most popular antiseptic, it is found in many disinfectant products (especially those used in hospitals).[7,8] 1-butanol is present in nature as a result of the fermentation of carbohydrates in some alcoholic beverages, such as beer, wine, whiskey.[9,10] 1-pentanol is a colorless liquid with an unpleasant odor and is used as a solvent for coating CDs and DVDs. 1-pentanol is a promising alternative fuel for use in diesel engines.[11,12]

RESULTS AND DISCUSSION

The experimental data obtained for binary mixtures: (propanoic acid + 1-propanol), (propanoic acid + 2-propanol), (propanoic acid + 1-butanol) and (propanoic acid + 1-pentanol) at 25°C are presented in tables 1 to 4. Figures 1 to 4 represent variation of V^E with x_1 (mole fraction of propanoic acid) at 298.15K. The excess molar volume was fitted with nonlinear Redlich – Kister equation with four parameters and results are presented in table 5. For the systems (propanoic acid + 1-propanol), (propanoic acid + 1-butanol) and (propanoic acid + 1-pentanol) the excess molar volumes decrease with increase of the alcohol concentration, passes through a minimum at about $x_2 = 0.5$ and then increases with increasing mole fraction of alcohol. This behavior is due to the fact that the hydrogen bond strength between the -OH and -COOH groups is higher than that of the same groups. On the other hand, the excess molar volume decreases with the increase of the length of the alcohol chain, this means that the strength of the hydrogen bond decreases.

For the binary mixture propanoic acid + 1-propanol the excess molar volume obtained in this work is -0.733 $cm^3 \cdot mol^{-1}$ at 25 °C at x_1=0.5, a value higher than that obtained in the literature -0.469 $cm^3 \cdot mol^{-1}$ at 30 °C but for a mixture of propanoic acid and 1-propanol dried and distilled.[13]

In the case of propanoic acid + 2-propanol system, at the molar fraction 0.5 of 2-propanol, the strength of hydrogen bonds, which is formed between one mole of alcohol and one mole of acid, is the strongest. At values of the mole fractions of 2-propanol less and greater than 0.5, the strength of hydrogen bonds decreases, because the molar ratio between alcohol and acid changes.[14] Therefore, if the strength of hydrogen bonds decreases, then the distance between the donor and the acceptor atom will increase, this will be reflected on the excess volume that will decrease. This phenomenon is most evident at $x_2 = 0,1$ (from Figure 2), because the strength of hydrogen bonds decreases most when propanoic acid is in excess.

In the case of the propanoic acid + 1-butanol systems, both the excess molar volumes and the partial molar volumes highlight the presence of attraction forces between the components for all molar fractions as shown in Table 3.

Table 1

Experimental data for propanoic acid (1) + 1-propanol (2) binary system

x_1	ρ_{mix} ($g \cdot cm^{-3}$)	V ($cm^3 \cdot mol^{-1}$)	V^E ($cm^3 \cdot mol^{-1}$)	$\overline{V}_1$ ($cm^3 \cdot mol^{-1}$)	$\overline{V}_2$ ($cm^3 \cdot mol^{-1}$)
1.0000	0.992	74.681	0.000	74.681	73.246
0.9003	0.975	74.532	-0.175	74.673	73.260
0.8006	0.958	74.421	-0.313	74.676	73.397
0.7008	0.940	74.321	-0.439	74.630	73.598
0.6009	0.923	74.234	-0.552	74.502	73.830
0.5010	0.906	74.079	-0.733	74.178	73.979
0.4009	0.886	74.167	-0.672	73.935	74.322
0.3008	0.866	74.246	-0.619	73.485	74.573
0.2006	0.845	74.424	-0.467	72.903	74.806
0.1003	0.824	74.641	-0.277	72.094	74.925
0.0000	0.802	74.944	0.000	71.070	74.944

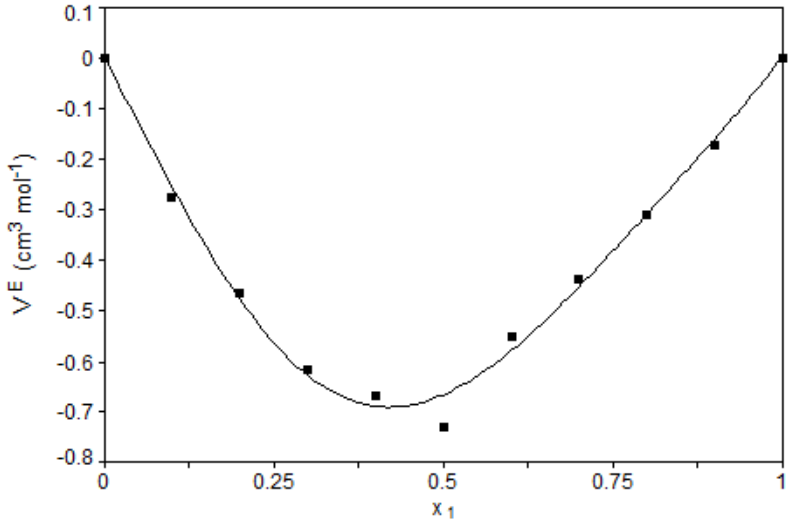

Fig. 1 – Redlich-Kister representation for propanoic acid + 1-propanol binary system.

Table 2

Experimental data for propanoic acid (1) + 2-propanol (2) binary system

x_1	ρ_{mix} (g·cm^{-3})	V (cm^3·mol^{-1})	V^E (cm^3·mol^{-1})	$\overline{V}_1$(cm^3·mol^{-1})	$\overline{V}_2$(cm^3·mol^{-1})
1.0000	0.992	74.681	0.000	74.681	81.310
0.9020	0.969	75.037	0.151	74.899	76.323
0.8036	0.950	75.087	-0.004	75.111	74.940
0.7047	0.932	75.049	-0.247	75.007	75.218
0.6054	0.912	75.172	-0.331	74.623	75.941
0.5057	0.892	75.300	-0.411	74.191	76.489
0.4054	0.870	75.599	-0.320	73.970	76.684
0.3048	0.848	75.855	-0.274	74.068	76.635
0.2036	0.827	76.088	-0.252	74.253	76.569
0.1021	0.806	76.356	-0.195	73.746	76.646
0.0000	0.783	76.764	0.000	71.011	76.765

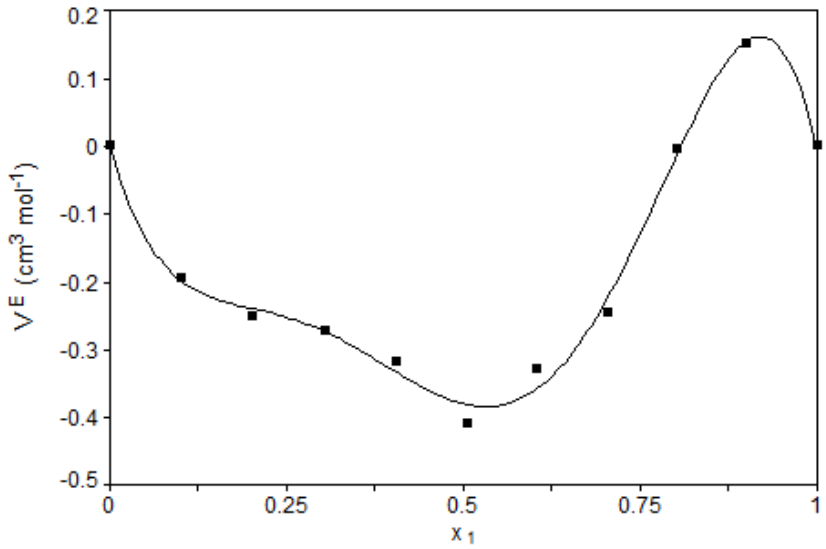

Fig. 2 – Redlich-Kister representation for propanoic acid + 2-propanol binary system.

Table 3

Experimental results for propanoic acid (1) + 1-butanol (2) binary mixture

x_1	ρ_{mix} (g·cm^{-3})	V (cm^3·mol^{-1})	V^E (cm^3·mol^{-1})	$\overline{V}_1$ (cm^3·mol^{-1})	$\overline{V}_2$ (cm^3·mol^{-1})
1.0000	0.992	74.692	0.000	74.696	89.963
0.9026	0.972	76.194	-0.150	74.680	90.277
0.8009	0.952	77.818	-0.252	74.629	90.571
0.7100	0.935	79.264	-0.346	74.553	90.804
0.5994	0.914	81.080	-0.407	74.424	91.050
0.5004	0.895	82.753	-0.413	74.273	91.234
0.3973	0.877	84.504	-0.410	74.080	91.391
0.3080	0.861	86.066	-0.363	73.884	91.498
0.1967	0.842	88.055	-0.262	73.602	91.593
0.1002	0.825	89.822	-0.132	73.323	91.642
0.0000	0.809	91.652	0.000	73.000	91.659

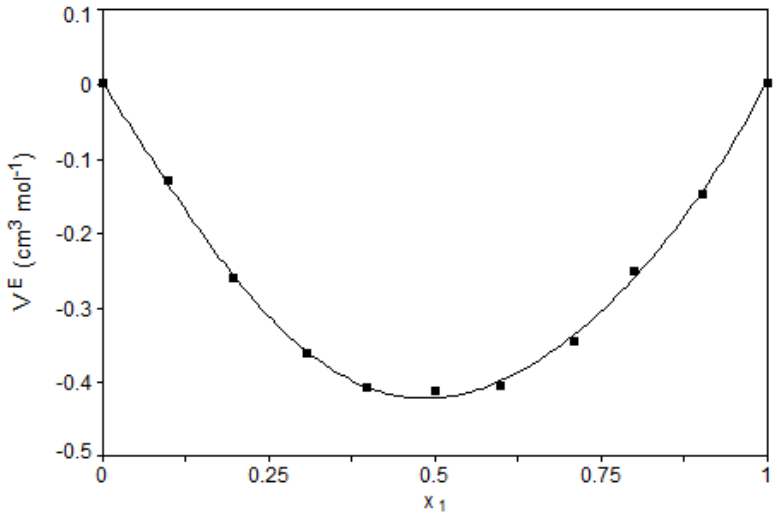

Fig. 3 – Redlich-Kister representation for propanoic acid + 1-butanol binary mixture.

Table 4

Experimental results for propanoic acid (1) + 1-pentanol (2) binary mixture

x_1	ρ_{mix} (g·cm^{-3})	V (cm^3·mol^{-1})	V^E (cm^3·mol^{-1})	$\overline{V}_1$ (cm^3·mol^{-1})	$\overline{V}_2$ (cm^3·mol^{-1})
1	0.992	74.661	0.000	74.632	106.959
0.9038	0.970	77.729	-0.184	74.618	107.235
0.7989	0.947	81.180	-0.276	74.571	107.504
0.6992	0.927	84.498	-0.329	74.496	107.730
0.5910	0.906	88.110	-0.374	74.380	107.940
0.4907	0.888	91.471	-0.404	74.241	108.104
0.4011	0.873	94.540	-0.364	74.091	108.224
0.3054	0.857	97.832	-0.303	73.905	108.326
0.2032	0.841	101.365	-0.227	73.675	108.405
0.0935	0.826	105.165	-0.133	73.393	108.454
0	0.813	108.460	0.000	73.124	108.467

For propanoic acid + 1-butanol system at x_1=0.5 the excess molar volume is similar with literature data (-0.421 $cm^3 \cdot mol^{-1}$).[13]

For propanoic acid + 1-pentanol system the excess molar volume decrease very little compared to propanoic acid + 1-butanol system. This means that the length of the chain no longer significantly influences the strength of the hydrogen bond.

The influence of the length of the alcohol chain on the molar excess volumes is shown in Fig. 5.

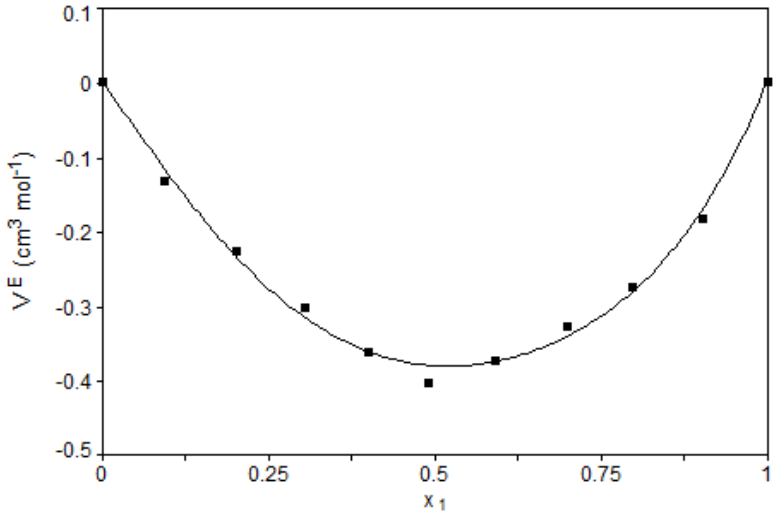

Fig. 4 – Redlich-Kister representation for propanoic acid + 1-pentanol binary system.

Table 5

The Redlich – Kister coefficients for all systems

System	A_0	A_1	A_2	A_3	R^2
propanoic acid+1-propanol	-2.6763	-1.1739	0.5685	0.8453	0.9898
propanoic acid+2-propanol	-1.5276	0.5116	1.9688	-4.6084	0.9923
propanoic acid + 1-butanol	-1.6947	-0.1080	0.1598	0.3138	0.9986
propanoic acid+1-pentanol	-1.5267	0.1067	-0.2143	0.3878	0.9927

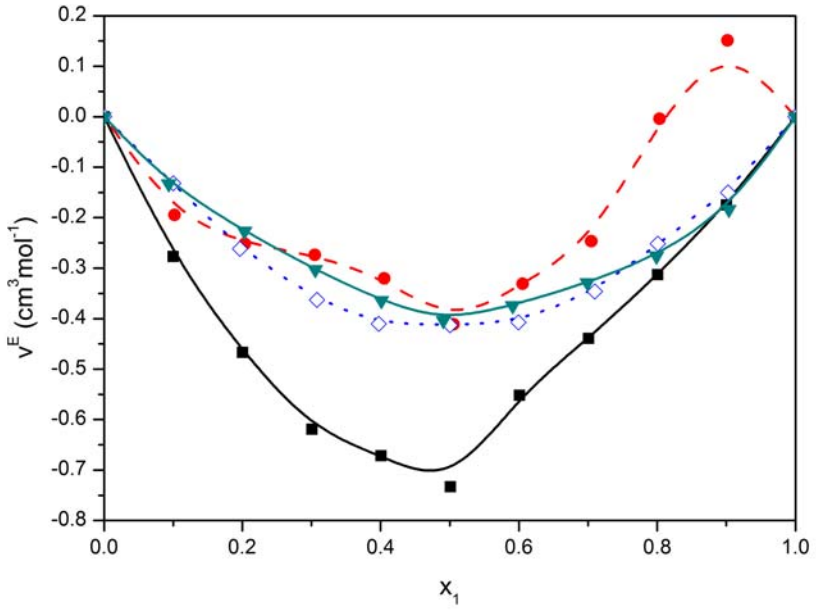

Fig. 5 – Excess molar volumes for binary systems: propanoic acid+1-propanol (■), propanoic acid+2-propanol (●), propanoic acid+1-butanol (◊) and propanoic acid+1-pentanol (▼).

From the experimental results it can be said that the strength of hydrogen bond decreases in order: propanoic acid +1-propanol, propanoic acid +1-butanol, propanoic acid +1-pentanol, propanoic acid +2-propanol which means it decreases with increasing the length of the alcohol chain and its branching.

EXPERIMENTAL

Materials. The propanoic acid (Loba Chemie, purity 99%), 1-propanol (Sigma-Aldrich, purity 99,7%), 2-propanol (Sigma-Aldrich, purity ≥ 99,5%), 1-butanol (Sigma-Aldrich, purity 99,8%) and 1-pentanol (Sigma-Aldrich, purity ≥ 99%) were used without further purification.

Apparatus and procedure. All binary mixtures were prepared by mixing the appropriate volume of liquids in a sealed glass vial to prevent evaporation. In this paper, the pycnometric method was used. [15] The density bottle (pycnometer) calibrated according to ISO 4787 with a volume of 10.334 cm^3. The pycnometer was filled with each binary solution and weighed with the Partner XA balance with a precision of 10μg. The experimental uncertainty in density was estimated to be less than ± $2 \cdot 10^{-5}$ $g \cdot cm^{-3}$.

The excess molar volumes for the binary mixtures were calculated using the formula:

$$V^E = \frac{(x_1 M_1 + x_2 M_2)}{\rho_{mix}} - (x_1 V_1^o + x_2 V_2^o)$$

where M_1 and M_2 are the molar masses of components 1 and 2, respectively,

ρ_{mix} the experimentally density of the liquid mixtures,

V_1^o and V_2^o are the molar volumes of the pure components,

x_1 and x_2 are the mole fractions

ρ_1 and ρ_2, are the density of pure components.

For each system, the partial molar volumes were calculated for alcohol ($\overline{V}_2$) and for acid ($\overline{V}_1$) respectively by the method of intercepts [16] with the relations:

$$\overline{V}_2 = V + x_1 \frac{\partial V}{\partial x_2}$$

$$\overline{V}_1 = V - x_2 \frac{\partial V}{\partial x_2}$$

The excess molar volume was determined by the difference between the molar volume and the ideal molar volume.[17-19] The excess molar volumes are fitted with the polynomial equations proposed by Redlich and Kister:[20-22]

$$V^E = x_1(1 - x_1) \cdot \sum_{i=0}^{n} A_i (1 - 2x_1)^i$$

where V^E is the excess molar volume and A_i represent semiempirical constants and n is degree of polynomial expansion.

CONCLUSIONS

The strength of the hydrogen bond decreases with increasing length of the alcohol chain, the excess volumes being smaller, except for the propanoic acid +2-propanol systems which have an atypical behavior.

For the systems propanoic acid +2-propanol, propanoic acid + 1-butanol and propanoic acid +1-pentanol, the excess volumes are approximately equal and highlight the presence of weak attraction forces due to the formation of hydrogen bonds.

The experimental data show that the strength of hydrogen bond decreases in the case of the propanoic acid +2-propanol mixture compared to the propanoic acid +1-propanol mixture due to the steric hindrance**.**

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