Excess molar volumes and excess molar enthalpies of binary mixtures for 1,2-dichloropropane + 2-alkoxyethanol acetates at 298.15 K

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Abstract

The excess molar volumes V_m^E and excess molar enthalpies H_m^E over the whole range of composition have been measured for the binary mixtures formed by 1,2-dichloropropane (1,2-DCP) with three 2-alkoxyethanol acetates at 298.15 K and atmospheric pressure using a digital vibrating-tube densimeter and an isothermal calorimeter with flow-mixing cell, respectively. The 2-alkoxyethanol acetates are ethylene glycol monomethyl ether acetate (EGMEA), ethylene glycol monoethyl ether acetate (EGEEA), and ethylene glycol monobutyl ether acetate (EGBEA). The V_m^E of the mixture has been shown positive for EGMEA, 'S-shaped' for EGEEA, being negative at low and positive at high mole fraction of 1,2-DCP, and negative for EGBEA. All the H_m^E values for the above mixtures showed an exothermic effect (negative values) which increase with increase in carbon number of the 2-alkoxyethanol acetates, showing minimum values varying from $-374 \, \text{J mol}^{-1}$ (EGMEA) to $-428 \, \text{J mol}^{-1}$ (EGBEA) around 0.54–0.56 mol fraction of 1,2-DCP. The experimental results of H_m^E and V_m^E were fitted to Redlich–Kister equation to correlate the composition dependence of both excess properties. In this work, the experimental excess enthalpy data have been also correlated using thermodynamic models (Wilson, NRTL, and UNIQUAC) and have been qualitatively discussed.
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1. Introduction

In recent years, a number of literatures of excess thermodynamic properties have been reported to provide useful information about molecular interactions and to test the thermodynamic models. According to our recent literature survey, few experimental values of excess properties for 2-alkoxyethanol acetates with halogenated hydrocarbon have been reported, except for binary mixtures of alkyl esters and α,ω-dichloroalkane [1,2].

Continuing our research program [3,4], this paper reports measurements of V_m^E and H_m^E of binary mixtures containing 1,2-dichloropropane (1,2-DCP) and three 2-alkoxyethanol acetates which are ethylene glycol monomethyl ether acetate (EGMEA), ethylene glycol monoethyl ether acetate (EGEEA), and ethylene glycol monobutyl ether acetate (EGBEA). These glycol ether esters have better solvent activity for coating resin

than ester or ketone solvents in their evaporation rate range [5].

1,2-DCP is a polar compound whose dipole moment is 1.87 debye (D) [6] at 25 °C, self-associated by dipole–dipole interaction. Breaking of this intermolecular attraction occurs upon mixing with highly polar 2-alkoxyethanol acetates which are also strongly self-associated compounds having dipole moment, 2.1 D for EGMEA, 2.2 D for EGEEA [6], not available for EGBEA. The chain length of 2-alkoxyethanol acetate must be taken into account to explain the behavior of 1,2-DCP and 2-alkoxyethanol acetate mixtures. The main characteristics of the compounds which are responsible for the deviations from ideality are polarity and self-association.

In our previous paper [4], excess properties of 1,2-dichloropropane + 2-(2-alkoxyethoxy)ethanol showed negative deviation from ideality due to the formation of weak hydrogen bonds between the hydrogen of 1,2-DCP and oxygen of 2-(2-alkoxyethoxy)ethanol at low mole fraction of 1,2-DCP, a relatively high energy then was needed to break intramolecular hydrogen bonds of 2-(2-alkoxyethoxy)ethanol at high mole fraction of 1,2-DCP.

The Redlich–Kister [7] equation has been fitted to both excess properties. The experimental H_m^E data were also used to test the suitability of Wilson, NRTL, and UNIQUAC models [8–10].

2. Experimental

2.1. Materials

Chemicals were obtained from Fluka (1,2-dichloropropane) and Sigma–Aldrich (2-alkoxyethanol acetates). The purity was at least 99% (except for EGEEA, whose purity was 98%). All reagents were used without further purification but degassed by means of an ultrasonic bath. In order to check purities of compounds, density ρ was measured by a vibrating-tube densimeter (model DMA-58, Anton Paar, Graz, Austria) equipped with an automatic sample changer (model SP3, Anton Paar, Graz, Austria) with a resolution $\pm 1 \times 10^{-5}$ g cm^{-3} and refractive indices n_D^{25} were measured by a refractometer (model RA-520, Kyoto Electronics, Japan) with an accuracy of ± 0.00001. Densities, refractive indices, and stated purities of the pure components are listed in Table 1 [6,11].

2.2. Apparatus and procedure

2.2.1. Density measurements

Densities ρ of pure components and their mixtures were determined with an Anton Paar DMA-58 densimeter with an accuracy $\pm 1 \times 10^{-5}$ g cm^{-3} operated in suction mode and equipped with automatic sample changer (model SP3). Mixtures were prepared by mass with a digital electronic balance (model AT-201, $\pm 1.0 \times 10^{-5}$ g, Mettler Toledo AG, Switzerland). The uncertainty of mole fraction of the mixture was estimated to be less than $\pm 1 \times 10^{-4}$. The densities, ρ of mixtures were used to calculate the excess molar volumes V_m^E according to:

$$V_m^E \,(\text{cm}^3\,\text{mol}^{-1}) = \frac{x_1 M_1 + x_2 M_2}{\rho} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} \quad (1)$$

where x_i, M_i and ρ_i, ρ are the mole fraction, molar mass, and density of component i, and density of mixtures, respectively. The estimated accuracy for the measurement of excess molar volume is $\pm 5 \times 10^{-4}$ cm^3 mol^{-1}.

Table 1
Densities ρ, refractive indices n_D, and stated purities of pure components at 298.15 K

Components	ρ (g cm^{-3})		n_D^{25}		Stated purities (%)
	Exptl.	Lit.[a]	Exptl.	Lit.[a]	
1,2-DCP	1.14895	1.14936	1.43653	1.43679	>99.0
EGMEA	0.99976	1.00033	1.39988	1.39990	>99.0
EGEEA	0.96736	0.96761	1.40311	1.40320	98.0
EGBEA	0.93512	0.94200[b]	1.41183	1.41360[b]	99.0

[a] Ref. [13], unless otherwise indicated.
[b] Ref. [6] and at 293.15 K.

2.2.2. Calorimetric measurement

Excess molar enthalpies were determined with an isothermal, heat-conduction, flow calorimeter (Calorimetry Sciences Corporation, CSC-4400, Utah, U.S.A) with a newly designed flow-mixing assembly kit (model CSC4442, Utah, U.S.A). Pressure in the calorimeter flow cell was fixed at 101.3 kPa by a back-pressure regulator (Grove valves & regulator Co., Stafford, TX, U.S.A) [12,13]. The magnitude of the measured heat signal is an important factor that has to be taken into account when selecting the total volumetric flow rate for a set of experiments; in this particular study, the selected value was 0.5 cm^3 min^{-1} for all the measurements.

The performance of the calorimeter has been examined by means of enthalpies of mixing for the systems {cyclohexane + n-hexane} (endothermic) and {water + ethanol} (exothermic) recommended as reference mixtures in isothermal calorimeters [14,15]. The comparisons were made both with results of Tanaka et al. [16] for the system {cyclohexane + n-hexane} and Chand and Fenby [17] and Costigan et al. [18] for the system {water + ethanol}. In all cases the smoothed result was within 1.6% of the previously published values [3].

The pure chemicals were pumped into the calorimeter with two digital HPLC pumps with a precision of $\pm 0.2\%$ (Acuflow Series II, Fisher Scientific, U.S.A). Each pump was calibrated by determining the volumetric flow rates from 0.01 cm^3 min^{-1} to 0.5 cm^3 min^{-1} of bi-distilled water and empirical correction equations were fitted for each pump. The determination of the mass of pumped water was measured with a digital electronic balance (model AT-201, $\pm 1.0 \times 10^{-5}$ g, Mettler Toledo AG, Switzerland). To eliminate the uncertainties in the volumetric flow rate, liquid components were kept double glass-lined jacketed bottles controlled by circulating coolant from a Haake temperature bath (PolyScience, 9100 Series, IL, U.S.A.). The newly designed flow-mixing cell is shown in Fig. 1. The calorimeter was calibrated electrically at 298.15 K by an auto-calibration mode and the temperature of the room was kept constant at (298.15 ± 0.5) K and relative humidity was controlled below 30% by glove box, which is equipped with air pump, desiccant cartridge, and hydrometer. The estimated accuracy for the excess enthalpy measurement is ± 0.7 J mol^{-1}.

Baseline values were determined by running pump I at total flow rate while pump II was turned off, then repeating with pump I off and pump II at the total flow rate. Baseline values Φ of each composition can be calculated according to following relation:

$$\Phi = \frac{\dot{q}_1 \dot{v}_1}{\dot{v}_T} + \frac{\dot{q}_2 \dot{v}_2}{\dot{v}_T} \quad (2)$$

where $\dot{q}_i$ is heat flux of component i and $\dot{v}_i$ and $\dot{v}_T$ are volumetric flow rate of components ($i = 1, 2$), and total flow rate, respectively. From volumetric flow rates, the molar masses (M_1 and M_2) and the densities (ρ_1 and ρ_2) of the pure components, the compositions (x_1 and x_2) of the mixture in the mixing cell, and the excess molar enthalpies can be determined by the relation of heat flux and the baseline value at each composition:

$$x_1 = \frac{\dot{v}_1 \rho_1 / M_1}{\{(\dot{v}_1 \rho_1 / M_1) + (\dot{v}_2 \rho_2 / M_2)\}} \quad (3)$$
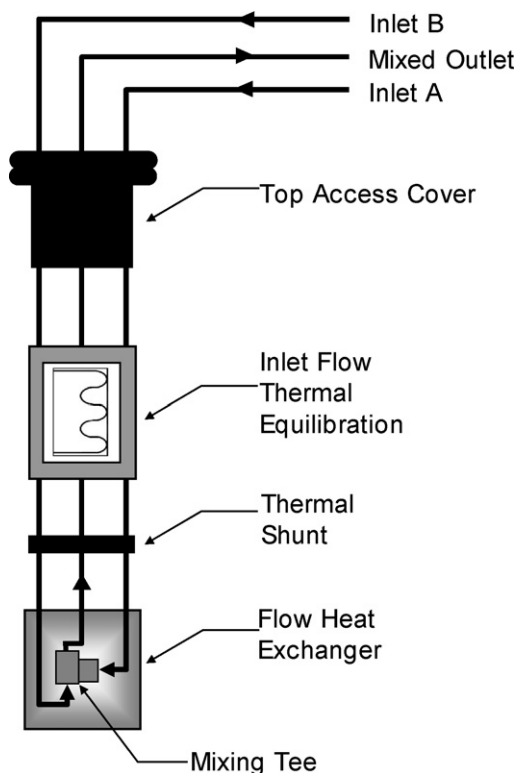
Fig. 1. Model 4442 flow-mixing cell (Calorimetry Sciences Corporation, UT).

$$H_m^E = \frac{\dot{q} - \Phi}{\{(\dot{v}_1 \rho_1 / M_1) + (\dot{v}_2 \rho_2 / M_2)\}} \tag{4}$$

where $\dot{q}$ is the heat flux upon mixing.

3. Results

The experimental values of V_m^E and H_m^E for the three binary systems $\{CH_2ClCHClCH_3(1) + CH_3COO(CH_2)_2O(CH_3)_n(2)\}$ ($n = 1$, 2 and 4) are listed in Tables 2 and 3 and shown in Figs. 2 and 3, respectively including curves fitted with Redlich–Kister equation. The experimental data of both V_m^E and H_m^E were correlated with Redlich–Kister polynomial by the method of unweighted least-squares:

$$Q_m^E \text{ (cm}^3\text{ mol}^{-1} \text{ or J mol}^{-1}) = x_1 x_2 \sum_{j=1}^{n} A_j (2x_1 - 1)^{j-1} \tag{5}$$

where both Q_m^E and A_j refer to either V_m^E or H_m^E, and x_1 is the mole fraction of 1,2-DCP. Values of the coefficients A_j, determined by a Nelder–Mead simplex pattern search method [19] using a commercial software package OriginPro 7.5, are given in Table 4 for both V_m^E and H_m^E along with standard deviations, σ:

$$\sigma = \left[\frac{\sum_{i=0}^{N} \{Q_m^E(\exp t) - Q_m^E(\text{calc})\}^2}{(N - n)} \right]^{1/2} \tag{6}$$

where N is the number of experimental points and n is the number of coefficients.

The experimental H_m^E data were also used to test the suitability of thermodynamic models (Wilson, NRTL, and UNIQUAC

Table 2
Excess molar volumes V_m^E for the binary mixtures of 1,2-DCP and 2-alkoxyethanol acetates at $T = 298.15$ K

x_1	V_m^E (cm^3 mol^{-1})	x_1	V_m^E (cm^3 mol^{-1})	x_1	V_m^E (cm^3 mol^{-1})
1,2-DCP (1) + EGMEA(2)					
0.0477	0.0111	0.3942	0.0593	0.7003	0.0495
0.0992	0.0244	0.4480	0.0613	0.7496	0.0430
0.1453	0.0372	0.5000	0.0602	0.7987	0.0354
0.1966	0.0443	0.5496	0.0587	0.8506	0.0293
0.2509	0.0497	0.5997	0.0566	0.8976	0.0204
0.2966	0.0545	0.6483	0.0536	0.9501	0.0099
0.3471	0.0570				
1,2-DCP (1) + EGEEA(2)					
0.0446	−0.0026	0.3974	0.0082	0.6978	0.0094
0.0924	−0.0036	0.4454	0.0098	0.7475	0.0075
0.1427	−0.0032	0.4983	0.0109	0.7943	0.0054
0.2032	−0.0015	0.5465	0.0116	0.8505	0.0031
0.2473	0.0009	0.5984	0.0113	0.8997	0.0017
0.2970	0.0027	0.6432	0.0107	0.9491	0.0007
0.3504	0.0056				
1,2-DCP (1) + EGBEA(2)					
0.0537	−0.0052	0.3982	−0.0308	0.7002	−0.0238
0.1015	−0.0105	0.4486	−0.0315	0.7495	−0.0188
0.1496	−0.0144	0.5023	−0.0316	0.8005	−0.0149
0.1999	−0.0188	0.5502	−0.0303	0.8585	−0.0107
0.2481	−0.0228	0.6023	−0.0281	0.8989	−0.0054
0.2970	−0.0261	0.6516	−0.0261	0.9505	−0.0015
0.3458	−0.0286				

Table 3
Excess molar enthalpy H_m^E for the binary mixtures of 1,2-DCP and 2-alkoxyethanol acetates at $T = 298.15$ K

x_1	H_m^E (J mol^{-1})	x_1	H_m^E (J mol^{-1})	x_1	H_m^E (J mol^{-1})
1,2-DCP (1) + EGMEA(2)					
0.0464	−58.8	0.4038	−342.9	0.7010	−339.4
0.0936	−105.7	0.4454	−357.1	0.7566	−312.2
0.1401	−152.8	0.5066	−370.5	0.8110	−266.0
0.2084	−214.1	0.5467	−374.6	0.8466	−229.8
0.2530	−251.1	0.6056	−370.5	0.8991	−168.1
0.2969	−281.8	0.6442	−361.5	0.9505	−90.9
0.3402	−312.9				
1,2-DCP (1) + EGEEA(2)					
0.0532	−73.2	0.3957	−373.8	0.6949	−367.7
0.1067	−126.6	0.4605	−396.4	0.7480	−332.4
0.1585	−199.3	0.5022	−403.1	0.7991	−287.7
0.2088	−248.5	0.5428	−404.9	0.8485	−236.4
0.2575	−289.9	0.6017	−398.5	0.8960	−175.4
0.3049	−323.2	0.6583	−387.5	0.9569	−82.9
0.3510	−352.0				
1,2-DCP (1) + EGBEA(2)					
0.0659	−94.3	0.4041	−395.6	0.7073	−382.4
0.0985	−124.9	0.4509	−409.0	0.7568	−347.6
0.1611	−208.6	0.4955	−420.0	0.8035	−304.3
0.1911	−228.1	0.5585	−428.1	0.8615	−238.0
0.2486	−286.3	0.5982	−424.7	0.9022	−180.5
0.3032	−330.7	0.6545	−409.1	0.9531	−94.4
0.3549	−367.8				

Table 4
Coefficients A_j of Redlich–Kister equation (Eq. (5)) and standard deviations σ (Eq. (6)), for representation of experimental V_m^E and H_m^E at 298.15 K and atmospheric pressure

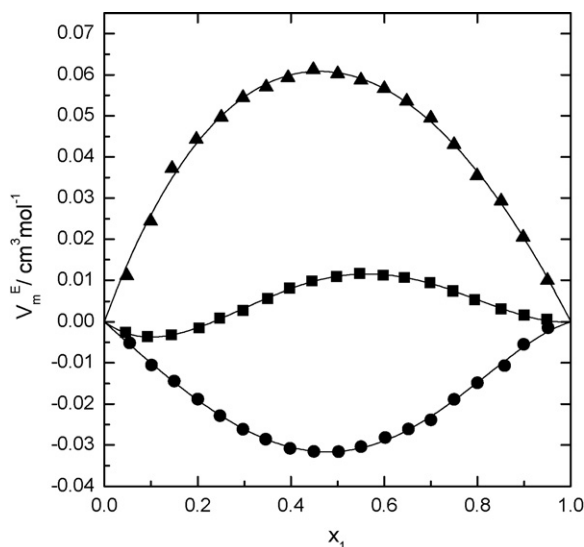| Excess properties	Binary systems	A_1	A_2	A_3	A_4	σ (cm^3 mol^{-1}/J mol^{-1})
V_m^E	1,2-DCP(1) + EGMEA(2)	0.2420	−0.0349	0.0223	−0.0086	0.0011
	1,2-DCP(1) + EGEEA(2)	0.0439	0.0346	−0.0876	0.0026	0.0002
	1,2-DCP(1) + EGBEA(2)	−0.1262	0.0154	0.0576	0.0193	0.0005
H_m^E	1,2-DCP(1) + EGMEA(2)	−1477.9	−325.6	−107.2	−68.8	1.9
	1,2-DCP(1) + EGEEA(2)	−1615.8	−242.2	−72.4	−77.0	3.4
	1,2-DCP(1) + EGBEA(2)	−1691.7	−341.1	−86.9	−22.4	3.1

Fig. 2. Excess molar volume, V_m^E of 1,2-dichloropropane(1) + 2-alkoxyethanol acetate(2) at 298.15 K. Experimental results: (▲) 2-methoxyethanol acetate; (■) 2-ethoxyethanol acetate; (●) 2-butoxyethanol acetate and (—) calculated with Eq. (5) using parameters listed in Table 4.
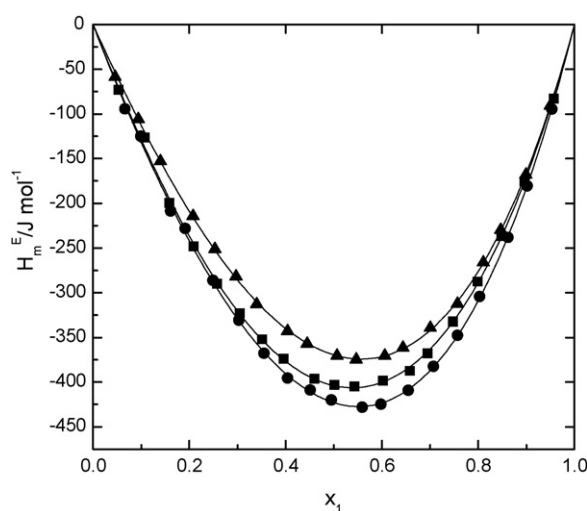

Fig. 3. Excess molar enthalpies, H_m^E of 1,2-dichloropropane(1) + 2-alkoxyethanol acetate(2) at 298.15 K. Experimental results: (▲) 2-methoxyethanol acetate; (■) 2-ethoxyethanol acetate; (●) 2-butoxyethanol acetate and (—) calculated with Eq. (5) using parameters listed in Table 4.

models) based on the local-composition theory for representing measured H_m^E data over the full range of compositions. The procedure is based on the rigorous Gibbs–Helmholtz equation written for excess properties:

$$H_m^E = -RT^2 \left[\frac{\partial (G^E/RT)}{\partial T} \right]_{P,x} \tag{7}$$

From Eq. (7), the experimental H_m^E data were fitted to the Wilson, NRTL, UNIQUAC models. This relationship can be derived by differentiating G^E/RT equations with respect to temperature according to the Gibbs–Helmholtz relation

to obtain a correlating equation for H_m^E as a function of temperature and composition. The adjustable parameters, $\lambda_{12} = a_{21} - a_{11}$ and $\lambda_{21} = a_{12} - a_{22}$ in the Wilson equation, $\tau_{12} = (g_{12} - g_{22})/RT$, $\tau_{21} = (g_{21} - g_{11})/RT$ and α in the NRTL equation, and $\Delta u_{12} = u_{12} - u_{22}$ and $\Delta u_{21} = u_{21} - u_{11}$ in the UNIQUAC equation are summarized in Table 5 together with the standard deviations. For the calculation of NRTL model, α value was fixed to 0.3 because of non-aqueous mixtures [20]. The Wilson, NRTL and UNIQUAC expressions for the excess enthalpy are given in Eqs. (8)–(10), respectively;

$$\frac{H_m^E}{x_1 x_2} = \frac{\lambda_{12} \Lambda_{12}}{x_1 + \Lambda_{12} x_2} + \frac{\lambda_{21} \Lambda_{21}}{x_2 + \Lambda_{21} x_1}, \tag{8}$$

Table 5
Adjustable parameters λ_{12} and λ_{21}, Wilson (Eq. (8)); τ_{12}, τ_{21} and α, NRTL (Eq. (9)); Δu_{12} and Δu_{21}, UNIQUAC (Eq. (10)) for calculating H_m^E derived at 298.15 K with standard deviations $\sigma(H_m^E)$

Systems	Adjustable parameters									
	Wilson			NRTL				UNIQUAC		
	λ_{12}	λ_{21}	σ (J mol^{-1})	τ_{12}	τ_{21}	α	σ (J mol^{-1})	Δu_{12}	Δu_{21}	σ (J mol^{-1})
1,2-DCP(1) + EGMEA(2)	−945.25	−284.28	2.03	0.22	−0.67	0.30	2.72	102.48	−490.10	2.24
1,2-DCP(1) + EGEEA(2)	−670.04	−758.97	3.50	0.01	−0.57	0.30	3.77	−257.93	−168.20	3.63
1,2-DCP(1) + EGBEA(2)	−532.44	−1032.33	3.17	0.09	−0.65	0.30	3.31	−410.48	25.23	3.12

where $\Lambda_{12} = V_2/V_1 \exp(-\lambda_{12}/RT)$ and $\Lambda_{21} = V_1/V_2\exp(-\lambda_{21}/RT)$, V_i is the molar volume of the component i,

$$\frac{H_m^E}{RTx_1x_2} = \frac{x_2 + x_1 \exp(\alpha\tau_{21})(1 - \alpha\tau_{21})}{\{x_1 \exp(\alpha\tau_{21}) + x_2\}^2}\tau_{21}$$
$$+ \frac{x_1 + x_2 \exp(\alpha\tau_{12})(1 - \alpha\tau_{12})}{\{x_2 \exp(\alpha\tau_{12}) + x_1\}^2}\tau_{12}, \qquad (9)$$

where α is the non-randomness parameter and $\tau_{12} = \Delta g_{12}/RT$, $\tau_{21} = \Delta g_{21}/RT$,

$$H_m^E = q_1 x_1 \left(\frac{\theta_2\tau_{21}\Delta u_{21}}{\theta_1 + \theta_2\tau_{21}}\right) + q_2 x_2 \left(\frac{\theta_1\tau_{12}\Delta u_{12}}{\theta_2 + \theta_1\tau_{12}}\right), \qquad (10)$$

where $\tau_{12} = \exp(-\Delta u_{12}/RT)$, $\tau_{21} = \exp(-\Delta u_{21}/RT)$ and $\theta_1 = x_1q_1/(x_1q_1 + x_2q_2)$.

4. Discussion

In Fig. 2, the dependence of excess molar volumes, V_m^E on compositions for three binary mixtures has been shown positive over the whole composition range for {1,2-DCP + EGMEA} and an 'S-shaped' form, being negative for poor and positive for rich component of 1,2-DCP for {1,2-DCP + EGEEA}, and negative in the entire composition range for {1,2-DCP + EGBEA}.

For the mixtures examined, changes in self-association (inter or intramolecular) and physical interaction (van der Waals interaction and dipole–dipole interaction) between like molecules increase the volume. On the other hand, free volume effects, interstitial accommodation or interactions between unlike molecules contribute to volume contraction. Our findings for {1,2-DCP + EGBEA}, that interactions among unlike molecules dominate over the other effects, are consistent with other research [21].

V_m^E decreases with an increase of chain length of 2-alkoxyethanol acetates. Since the polarity increases with an increase of chain length, a decrease in V_m^E due to the dipole–dipole interaction between unlike molecules can also be observed.

The cross-association between the unlike molecules, however, becomes dominant over the self association as soon as the 1,2-DCP is mixed with EGBEA due to less steric interaction between the unlike molecules. EGBEA is large in size, and creates open space when the molecules are self-associated. Accordingly, the open space may accommodate 1,2-DCP because of the unlike dipole–dipole interaction and van der Waals attraction force. As a result, the negative value of V_m^E was observed.

This conclusion, however, is not true for the mixture of 1,2-DCP and lower 2-alkoxyethanol acetates. Like the binary system between $CH_3(CH_2)_{n-1}OH$ ($n = 4$–8) and $CH_3(CH_2)_3Cl$ [22], the maximum value of V_m^E decreases as the chain length of 2-alkoxyethanol acetate increases, indicating a lower steric interaction among the long carbon chain of 2-alkoxyethanol acetate in order to introduce the molecules of 1,2-DCP. The addition of 1,2-DCP as a solute into EGMEA (lower carbon of 2-alkoxyethanol acetates) is comparatively difficult due to the appreciable amount of steric interaction between the 1,2-DCP and EGMEA. The

opposing effect consisting of intermolecular association produced by the formation of weak hydrogen bonds between the –COO– group of EGMEA and hydrogen on the 1,2-DCP has no significance. Due to this, the dipole–dipole interaction among the unlike molecules is less effective, which leads to the volume expansion and ultimately brings about the positive contribution to the V_m^E for the whole composition range of 1,2-DCP.

In the case of {EGEEA + 1,2-DCP}, the steric hindrance effect between unlike molecules lies in between the aforementioned mixtures. That is why this binary mixture gives both positive (most region of 1,2-DCP) and negative (only in poor 1,2-DCP region.) values of V_m^E.

The curves of excess molar enthalpy versus composition are all nearly symmetrical over the entire experimental conditions and maximum negative values are (-374.62, -404.89, -428.11 Jmol^{-1}) for EGMEA at ($x_1 = 0.547$), EGEEA at ($x_1 = 0.54$), and EGBEA at ($x_1 = 0.55$), respectively. At equimolar composition of the 1,2-DCP, negative H_m^E values follow the sequence:

EGBEA > EGEEA > EGMEA.

Usually, the H_m^E are negative when the interaction between the unlike molecules are stronger than that of like molecules and vice-versa [23]. The experimental results of the H_m^E indicate that interaction between 1,2-DCP and 2-alkoxyethanol acetates is stronger than the total interaction of 1,2-DCP-1,2-DCP and 2-alkoxyethanol acetate-2-alkoxyethanol acetate. This order reveals that negative excess enthalpies increase with an increase in chain length of 2-alkoxyethanol acetates. This effect can be interpreted on the basis of solvent polarity. The dipole moment of 2-alkoxyethanol acetates shows that the polarity of the compounds also increases with an increase in chain length. 1,2-DCP is also a polar compound but it is less polar than 2-alkoxyethanol acetates. The effect of the presence of 1,2-DCP in the system can be explained by considering the 1,2-DCP as the solute and 2-alkoxyethanol acetates as the solvent. Since 1,2-DCP is smaller than each of the 2-alkoxyethanol acetate compound, admission of 1,2-DCP into the environment of 2-alkoxyethanol acetate compounds occurs easily. As soon as the 1,2-DCP (polar compound) is mixed with these 2-alkoxyethanol acetates, a strong dipole–dipole interaction between –COO– group of 2-alkoxyethanol acetates and hydrogen on the 1,2-DCP is more pronounced than the dissociation effect of the 2-alkoxyethanol acetates. As a result, energy is released during this mixing process causing a negative deviation from the ideality.

5. Conclusion

Both V_m^E and H_m^E decrease as the carbon number of 2-alkoxyethanol acetates increases. H_m^E values of all binary mixtures are negative for the whole composition range, due to the predominant effect of dipole–dipole interaction between the unlike molecules. But the V_m^E of the mixture has been shown to be positive over the whole composition range for EGMEA, slightly negative only in the poor 1,2-DCP region for EGEEA and negative over the entire composition range of 1,2-DCP for EGBEA.

The positive V_m^E value for the binary mixture containing 1,2-DCP and EGMEA throughout the composition range is due to the effective steric interaction between the unlike molecules.

The Redlich–Kister polynomial equation successfully correlates both the experimental H_m^E and V_m^E data. For all mixtures, a good agreement between experimental H_m^E and calculated H_m^E by using Wilson, NRTL, and UNIQUAC models was obtained. Of the three models, Wilson equation was found to be most appropriate for correlating the enthalpy of mixing data than either NRTL or UNIQUAC model for all systems except EGBEA. For the binary mixture of 1,2-DCP with EGBEA, UNIQUAC model was slightly better than the other models.

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